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## PREFACE

The fourth volume of the Annual Review of Physical Chemistry is organized in essentially the same subdivisions as have been used in the earlier volumes. The subject of contact catalysis and surface chemistry which was omitted last year is included again. New topics are represented by the reviews of magnetism and of microwaves and nuclear resonance. It is not expected that such subjects will be reviewed every year but rather that the frequency of review will depend on the interest in the field as indicated by the number of papers published. The reader will note that neither of these topics can be assigned readily to a place under one of the broader titles reviewed each year. The editors are anxious to have as complete coverage as possible of the entire field of physical chemistry and will welcome suggestions of other topics of this type which may be reviewed from time to time. The omission for the second successive year of the review of colloids arises because of conditions beyond our control and should not be construed as indicating a lack of interest in such work.

At this time we wish to give public expression of our thanks to the authors who have co-operated in the preparation of this volume. The many favorable comments we have received concerning previous volumes indicate that these efforts are also greatly appreciated by physical chemists throughout the world. We hope that in the future we will continue to receive the co-operation of such able scientists.

B.L.C.	W.F.L.
G.E.K.	J.W.W.
J.G.K.	R.E.P.
G.K.R.	



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# THERMOCHEMISTRY AND THE THERMODYNAMIC PROPERTIES OF SUBSTANCES<sup>1</sup>

By J. W. STOUT

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Although the general thermodynamic principles and the techniques of measurement of what are called thermodynamic properties have been well established for many years, the field of thermochemistry and the thermodynamic properties of substances continues to attract many investigators. In addition to the importance of free energy and heat data for the investigation of the stability of chemical compounds and equilibrium in chemical reactions, the use of thermodynamic methods is a valuable tool in understanding many diverse phenomena. Because of limitations of space it has not been possible to include in this review all topics of thermodynamic interest. No survey is given of work on adsorption and the thermodynamics of surfaces, on solutions, on bond energies, or on isotopic equilibria. Work in some of these fields is reviewed elsewhere in this volume.

*Physical constants and tabulations of data.*—A committee of the National Research Council [Rossini *et al.* (1)] has considered and selected best values of the fundamental constants needed in physical chemistry. The Bureau of Standards circular, *Selected Values of Chemical Thermodynamic Properties*, compiled under the direction of Rossini & Wagman (2), has now been issued in a bound volume. This work, which runs to 1268 pages, is a critical selection of best, and internally self-consistent, values of thermodynamic properties for all chemical substances except carbon compounds containing more than two carbon atoms. The tables of Series I list the heat of formation at 0°K., and heat and free energy of formation, entropy, and heat capacity at 298.16°K. In Series II are given values of pressure, temperature,  $\Delta H$ ,  $\Delta S$ , and  $\Delta C_p$  for processes of solid transition, fusion, vaporization, and sublimation. Complete literature references are given. The tables of Series III, which list the thermodynamic properties at a number of temperatures, are not included in the bound volume and have appeared only as loose sheets without references.

## DATA OF STATE FOR GASES, LIQUIDS, AND SOLIDS

For some time Beattie and co-workers at the Massachusetts Institute of Technology and Michels and co-workers at the University of Amsterdam have been making accurate pressure-volume-temperature measurements on gases. In the year 1952 data on several substances were reported from each of these laboratories. Beattie, Douslin & Levine (3) have investigated the compressibility of gaseous neopentane from its critical temperature (160.6°C.)

<sup>1</sup> The survey of the literature pertaining to this review was concluded in December, 1952.

to 275°C. and at densities of from one to seven moles per liter. Similar measurements on *n*-pentane were made by Beattie, Levine & Douslin (4). In each case the constants of the Beattie-Bridgeman equation of state and values of the second virial coefficient were calculated from the experimental data. Beattie, Brierley & Barriault (5, 6) have made compressibility measurements on gaseous krypton at temperatures from 0 to 300°C. and at densities from one to ten moles per liter. It was found that values of the second virial coefficient calculated from these data agreed with those predicted by a Lennard-Jones interatomic potential function with a sixth-power attractive term and a twelfth-power repulsive term. The two parameters in the Lennard-Jones potential were chosen to give the best fit to the observed second virial coefficients. The experimental values of the third virial coefficient were, however, about twice as large as those calculated.

Michels *et al.* (7) report compressibility data on CH<sub>3</sub>F from 0 to 150°C. and at pressures up to 150 atm. Data for CO over the same temperature range and at pressures up to 3000 atm. are given by Michels *et al.* (8). In both cases values of internal energy, entropy, and heat capacity, derived from the compressibility data combined with heat capacities of the low pressure gas, are tabulated. An extensive summary of the thermodynamic properties of nitrogen in the temperature range from -125 to 150°C. and at pressures up to 6000 atm. has been given by Lunbeck, Michels & Wolkers (9). Hamann & Pearse (10) have measured second virial coefficients of CH<sub>3</sub>Br, CH<sub>3</sub>Cl, CH<sub>3</sub>F, and cyclopropane. They find that the results may be fitted by a 6-12 Lennard-Jones potential function and do not require the use of a nonspherically symmetrical potential as might be expected for permanent dipoles. They conclude that the molecular rotation causes a polar molecule to behave like a sphere. Other values of second virial coefficients are: Korveze (11), C<sub>6</sub>H<sub>6</sub>; Francis *et al.* (12), C<sub>6</sub>H<sub>6</sub>; Fox & Lambert (13), mixed organic vapors; Casado, Massie & Whytlaw-Gray (14), (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O, CCl<sub>4</sub>, CS<sub>2</sub> and perfluoromethylcyclohexane. The last named authors were principally interested in the limiting *PV* product at zero pressure for molecular weight determination, but from the slope of *PV* versus *P* a value of the second virial coefficient may be obtained. It is interesting to note that for acetone at 22°C., even in the range of 20 to 150 mm. pressure, there is a serious curvature in the graph of *PV* versus *P*, indicating that the gas imperfection in this gas cannot be adequately represented by a single virial coefficient.

*Theoretical calculations of equation of state.*—Fickett & Wood (15) have made numerical calculations of the Lennard-Jones and Devonshire equation of state in the region of high temperatures and densities. Hamann (16) has calculated corrections to this equation of state by quantizing the translational motion within individual molecular cages. By comparison with experimental data he finds that this procedure overcorrects for quantum effects. Roe, Epstein & Powers (17) and Epstein & Hibbert (18) calculate second virial coefficients for a 6-9 Lennard-Jones potential and Epstein (19) derives



## THERMOCHEMISTRY

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an asymptotic form valid at low temperatures for a 6- $s$  potential, where  $s$ , the coefficient of the repulsive term, may be arbitrarily chosen. No correction is made for quantum effects. Cottrell & Paterson (20) have calculated an equation of state applicable to gases at densities comparable to solid densities and at high temperatures. Mayer & Careri (21) have discussed equation of state computations at high densities. They suggest a logical computation method which involves making exact calculations of the Helmholtz free energy for the nonequilibrium system and then finding the equilibrium state by minimizing this free energy at constant volume and temperature. The method resembles the cell method of Lennard-Jones and Devonshire, but with cells of variable size, and is numerically easier and more exact than previous applications of the cell method. Himpan (22) has proposed a new empirical equation of state.

*Critical phenomena.*—A very interesting series of Canadian papers has clarified the experimental situation regarding the "flat top" in liquid-vapor coexistence curves at the critical point. It is found experimentally that the temperature at which the liquid-vapor meniscus is seen to disappear in a long vertical tube is the same throughout an appreciable range of overall density. This has been interpreted as indicating that there does not exist a unique critical temperature and density, a question of considerable theoretical interest. Because of the very large isothermal compressibilities in the critical region, however, a fluid which has a unique critical temperature will in a gravitational field exhibit large equilibrium density gradients. For a given overall density there will be a certain height in the tube which at the critical temperature has the correct critical density and at this position the meniscus will disappear. For other densities the correct critical density will be reached at a different position in the tube, but the disappearance of the meniscus will still occur at the critical temperature. Thus in a long vertical tube the critical temperature will seem, because of the gravity effect, to be constant over a wide range of density. Weinberger & Schneider (23) observed that in a vertical tube 19 cm. long there was an appreciable horizontal portion in the curve of temperature versus overall density for xenon in the critical region, but when the tube was laid on its side so that its height was 1.2 cm. the flat-top portion was not detectable. Using a radioactive tracer technique, these authors (24) have also investigated the equilibrium density gradients in a vertical tube of xenon near its critical temperature and find a considerable density gradient consistent with the calculated effect of gravity. Murray & Mason (25) have investigated by means of light scattering the density gradients near the critical temperature of ethane and conclude that the observed gradients can explain the flat portion of the liquid-vapor coexistence curve. Weinberger, Habgood & Schneider (26) have measured isotherms of xenon in a short bomb and agree that gravitational effects are capable of explaining the whole of the flat-top width of observed coexistence curves. Zimm (27) has pointed out that the experimental data of Rowden & Rice (28) on the two-liquid system aniline-cyclohexane

are as consistent with a coexistence curve cubic in the composition difference from the maximum as with the flat-topped curve proposed by the authors.

Using a correlation liquid model, Goldstein (29) has shown theoretically that for a normal monatomic liquid there is at the critical temperature a condensation in the space of relative momenta somewhat analogous to the condensation of a Bose-Einstein fluid in ordinary momentum space. Alder & Jura (30) have reconsidered the old question of the possibility of a solid-gas critical temperature. They calculate that a critical point should exist for solid helium at about 90°K. and 29,000 atm. pressure.

Anderson *et al.* (31) report experimental critical constants of  $\text{OF}_2$ .

*Transitions in solids.*—Stephenson, Blue & Stout (32) report low temperature heat capacity measurements on  $\text{NH}_4\text{Cl}$  and  $\text{ND}_4\text{Cl}$ . In both compounds the entropy change associated with the gradual transition is about  $R \ln 2$ , indicating that the transition is from an ordered low temperature state to a high temperature state in which each ammonium ion may occupy two positions of nearly equal energy. The crystal structure as determined from neutron diffraction measurements by Levy & Peterson (33) confirms this interpretation. Stephenson, Landers & Cole (34) have found that the gradual transition near 231°K. in  $\text{NH}_4\text{I}$  is similar to that in  $\text{NH}_4\text{Cl}$ , but the heat capacity data indicate that above the first order transition occurring at 257°K., corresponding to a change from the  $\text{CsCl}$  to the  $\text{NaCl}$  lattice, the ammonium ions are rotating. Transition temperatures of solid solutions of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  and a new transition in  $\text{NH}_4\text{Br}$  are reported by Stephenson & Adams (35). Kondo & Oda (36) have made dilatometric and thermal measurements of two phase transformations in barium dicalcium *n*-butyrate, and Powles (37) has given a general theoretical discussion of the phase changes in the solid hydrogen halides. The papers and discussions of the 1948 Cornell symposium on phase transformations in solids have been published in book form (38). The articles in this monograph, written by leading authorities, provide an excellent summary of both the theoretical and experimental knowledge about phase transformations.

*Vapor pressures, heats of vaporization and fusion.*—Additional references on vapor pressures and heats of fusion, transition, and vaporization will be found in the section on Heat Capacities, Heat Contents, and Entropies, since accurate measurement of these quantities is often made in an entropy determination. References to papers primarily concerned with vapor pressure are (a) Elements: Michels, Wassenaar & Zwietering (39), Kr; Brooks (40), Te and Se; Edwards, Johnston & Blackburn (41), Mo; Gulbrandsen & Andrew (42), Cr; Searcy (43), Ge. (b) Inorganic compounds: Burns & Dainton (44),  $\text{NOCl}$ ; Schnizlein *et al.* (45),  $\text{OF}_2$ ; Schäfer and co-workers (46, 47, 48),  $\text{FeCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{NbCl}_5$ ; Junkins and co-workers (49, 50),  $\text{NbF}_5$  and  $\text{TeF}_4$ ; Jolly & Latimer (51),  $\text{GeI}_4$ ; Shapiro (52),  $\text{ThO}_2$ . (c) Organic compounds: Michels, Wassenaar & Zwietering (53), CO; Allen, Everett & Penney (54),

$C_6H_6$ ; Edwards (55), tetranitromethane; Day & Felsing (56), 3-methylpentane (also liquid compressibility); Milton & Oliver (57), *n*-hexadecafluoroheptane (also critical constants); Stiles & Cady (58), perfluoro-*n*-hexane and perfluoro-2-methylpentane. In most cases, heats of vaporization are calculated from the vapor pressure data. In cases where the free energy of the gas can be calculated from molecular data and that of the solid from thermal data and the third law of thermodynamics, a value of the enthalpy of vaporization may be obtained from each vapor pressure point. The constancy of the values of  $\Delta H_0^\circ$  obtained over a range of temperatures is a sensitive test of the consistency of the data and, if there is no significant trend in the values, a much more precise value for the heat of vaporization may be obtained than is possible from the slope of a  $\log P$  versus  $1/T$  curve. For example, in the case of molybdenum (41) the mean deviation in the value (155.55 kcal.) of  $\Delta H_0^\circ$  was 0.19 kcal.

The question of the vapor pressure and heat of vaporization of graphite remains unsettled. Doehaerd, Goldfinger & Waelbroeck (59, 60) have made measurements of evaporation rates from a crucible in which the ratio of evaporating area to orifice was 24,000. They obtain a heat of vaporization consistent with the spectroscopic value of 141 kcal, and conclude that the sticking coefficient of C atoms is very low and that consequently the value of 170 kcal. obtained by Brewer, Giles & Jenkins (61) for the heat of vaporization is too high. This conclusion has been questioned by Brewer (62) who emphasizes the importance of volatile impurities in graphite which give a high vapor pressure and consequently a low heat of vaporization. Farber & Darnell (63) report measurements of the evaporation rate from a graphite filament, but in the absence of knowledge of the sticking coefficient cannot determine the vapor pressure.

Brown (64) discusses vapor pressure curves and the Hildebrand rule, and Simons & Hickman (65) suggest empirical equations correlating energy of vaporization with polarizability. The heat of fusion of lithium has been measured by Kilner (66).

#### HEAT CAPACITIES, HEAT CONTENTS, AND ENTROPIES

Jura & Pitzer (67) discuss theoretically the specific heat of small particles at low temperatures. For the case of cubes of aluminum, 100 Å on an edge, the contribution of the translation and rotation of the crystals, which is independent of temperature, is, below 3°K., larger than the vibrational heat capacity. Law (68) also discusses the surface contribution to the heat capacity of solids.

*Inorganic substances.*—Values of low temperature heat capacities, heat contents, and third law entropies are: Hu & Johnston (69), CuBr; Adams & Johnston (70),  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>; Oliver & Grisard (71), BrF<sub>3</sub> (also vapor pressure data); Todd & Coughlin (72), TiS<sub>2</sub> (also high temperature heat content data); Todd & Lorenson (73), Ba<sub>2</sub>TiO<sub>4</sub>, Sr<sub>2</sub>TiO<sub>4</sub>, and an equimolal solid solution;

Todd (74),  $\text{Mg}_2\text{TiO}_4$  and  $\text{Mg}_2\text{Ti}_2\text{O}_5$ ; Todd & Lorenson (75),  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$ , and a solid solution; Jones, Gordon & Long (76), U,  $\text{UO}_2$ , and  $\text{UO}_3$ ; Rubin & Giauque (77),  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , and  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (also heat of fusion); Kunzler & Giauque (78),  $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  glass and crystals (also heat of fusion); Busey & Giauque (79),  $\text{NiCl}_2 \cdot \text{UO}_2$  and  $\text{NiCl}_2$  exhibit peaks in heat capacity at low temperatures, almost certainly associated with an antiferromagnetic ordering of the atomic magnetic moments. Unlike crystalline ice, crystals of sulfuric acid and its mono-, di-, and tri-hydrate all approach an ordered state of zero entropy at low temperatures. The disorder in sulfuric acid trihydrate glass at  $0^\circ\text{K}$ . corresponds to 5.9 e.u. The ferroelectric material  $\text{BaTiO}_3$  shows small peaks in heat capacity at temperatures corresponding to anomalies in dielectric behavior, but the corresponding anomalous entropy changes are less than 0.1 e.u., showing that there is no appreciable change in order. Friedberg (80) has measured heat capacities of the antiferromagnetic material  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  between 1.5 and  $20^\circ\text{K}$ . There is a maximum in heat capacity at  $4.31^\circ\text{K}$ ., and at this temperature the vibrational heat capacity is so small that accurate correction may be made for it. About one-third of the total magnetic entropy of  $R \ln 2$  appears at temperatures above the heat capacity maximum. Measurements of the heat capacity of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  between 0.25 and  $3^\circ\text{K}$ ., as well as the isentropic change in temperature and intensity of magnetization with magnetic field, are reported by Geballe & Giauque (81). There is an anomaly in the heat capacity curve with maxima near  $1.3^\circ\text{K}$ . About half of the total magnetic entropy of  $R \ln 2$  is lost at a temperature of  $0.25^\circ\text{K}$ ., and below this temperature the heat capacity is rising again. The detailed shape of the heat capacity curve is very unusual and cannot be explained by any existing theories of antiferromagnetism or crystalline field splitting.

*Organic substances.*—The thermodynamics laboratory of the Bureau of Mines station at Bartlesville, Oklahoma has contributed a number of important papers. The group there, which was originally established under the direction of the late Hugh M. Huffman, is making precise thermodynamic measurements on a number of prototype organic compounds in order to establish a large body of data from which generalizations may be made concerning reactions of interest to the petroleum industry. Measurements are made of low temperature heat capacities, heats of transition, fusion, and vaporization, and vapor pressures. The gas imperfection is estimated from the Clapeyron equation,  $dP/dT = \Delta H / (T \Delta V)$ , using experimental values of the heat of vaporization and vapor pressure. In some cases measurements are made of vapor heat capacities, and the isothermal change of heat capacity with pressure is used, through the thermodynamic relation  $(\partial C_p / \partial P)_T = -T(\partial^2 B / \partial T^2)$ , to correlate the second virial coefficients,  $B$ , over a range of temperature. The molecular constants of the gaseous molecules are estimated (some new infrared data is reported). The third law entropy and vapor heat capacities are used to fix unobservable vibrational

frequencies and barriers hindering internal rotation. The thermodynamic functions  $(F^\circ - H_0^\circ)/T$ ,  $(H^\circ - H_0^\circ)$ ,  $S^\circ$  and  $C_p^\circ$  of the gaseous molecules are tabulated up to 1000 or 1500°K. Some measurements of heats of formation are reported. Papers appearing in 1952 are: Scott *et al.* (82), 2,2,3,3-tetramethylbutane (83), 3,4-dithiahexane; Guthrie *et al.* (84), thiacyclopropane; McCullough *et al.* (85); ethanethiol; Finke *et al.* (86), 1-pentanethiol; Scott *et al.* (87), 3-thiapentane; Guthrie *et al.* (88), furan; Hubbard *et al.* (89), thiacyclopentane. Other measurements of heat capacities and entropies are: Stephenson & Berets (90), melamine and dicyandiamide; Furukawa, McCoskey & King (91), polytetrafluoroethylene. Pomerantz (92) describes the synthesis and physical properties of *n*-heptane for use as a calorimetric standard (93) for heat capacity.

*Metals.*—Douglas *et al.* (94) have measured heat capacities of potassium and sodium-potassium alloys in the range 0–800°C. Measurements of heat capacity in the range from 15°K. to room temperature are: Busey & Giaque (95), Ni; Geballe & Giaque (96), Au; Adams, Johnston & Kerr (97), Ga (including heat of fusion); Clusius & Schachinger (98), Co. Hill & Parkinson (99) have measured low temperature heat capacities of Ge and grey Sn, and Pearlman & Keesom (100) report data for Si. The deviations from the Debye curve of the heat capacities of the isomorphous structures diamond, Si, Ge, and grey Sn are similar in that all show a minimum in the apparent Debye  $\theta$  at temperatures slightly below one-tenth of the high temperature  $\theta$ -value. Even on a reduced scale of temperature, however, there are important quantitative differences between the four curves.

Considerable work has appeared on the heat capacity of metals in the temperature range of liquid helium. At these temperatures the vibrational heat capacity, which varies as  $T^3$ , has become small enough so that the electronic heat capacity, which is proportional to the temperature, is an appreciable fraction of the total. In the expression  $C(\text{electronic}) = \gamma T$  for the heat capacity arising from electronic excitation, the coefficient  $\gamma$  is proportional to the density of electronic energy states at the top of the Fermi surface. In the transition metals  $\gamma$  is high because of the high density of states in the unfilled *d*-bands. Calorimetric measurements from which values of  $\gamma$  have been obtained include: Clement & Quinell (101), In; (102), Pb; Brown, Zemansky & Boorse (103), Nb; Horowitz *et al.* (104), Pb; Keesom & Pearlman (105), Ag; Estermann, Friedberg & Goldman (106, 107), Cu, Mg, Ti, Zr, Cr. Of particular interest are the results on chromium, which has an electronic heat capacity much smaller than the neighboring elements of the first transition series. Values of  $\gamma \times 10^4$  in cal. deg<sup>-2</sup> mole<sup>-1</sup> are Ti, 8.0; V, 15; Cr, 3.8; Mn, 42; Cu, 1.80. The low value found for the density of electronic states in chromium would be expected on Zener's (108) theory of ferromagnetism which predicts that the spins of the *d*-electrons in chromium are ordered in an antiferromagnetic fashion. In such a case the *d*-band will be split into two halves, with the lower half completely filled and

the upper half empty. The contribution to the electronic heat capacity will then be due only to excitation of electrons in  $s$  and  $p$  bands. However, theoretical calculation of band shapes by Slater (109) and by Fletcher & Wohlfarth (110) indicate that even without an antiferromagnetic ordering the density of states is small near the middle of the  $d$ -band and the observed value for chromium is consistent with their calculations.

From measurements of critical magnetic field curves for superconductors one can deduce the difference in heat capacity between normal and superconducting states, provided the magnetic transition is reversible. Since no term linear in temperature has been observed in the heat capacity of a superconducting metal, the linear term in the difference is identified with the electronic heat capacity of the normal metal. The values so deduced are in fair agreement with those obtained calorimetrically except in the case of the "hard" superconductors which have high melting points. Wexler & Corak (111), by special attention to purity and thermal treatment, have obtained samples of vanadium with nearly reversible magnetic properties and conclude that the source of the disagreement lies in irreversibility in the magnetic properties caused by internal strains and impurities. Other values of  $\gamma$  deduced from magnetic data are given by Goodman (112), Al, Cd, Ga, Zn, Ru, Os; Smith & Daunt (113), Cd, Zr, Hf, Ti; Stout & Guttman (114, 115), In-Tl solid solutions and MgTl; Love, Callen & Nix (116), In-Tl solid solutions. In the case of the In-Tl alloys the magnetic transitions are reversible in the dilute solutions, but become less so as the concentration of thallium increases.  $\gamma$  changes little with composition as one might expect from the similarity in electronic structure of In and Tl. Although the transition temperatures of superconducting isotopes vary inversely as the square root of the isotopic mass, there is no change in the electronic heat capacity of the normal metal. Measurements on Sn isotopes are reported by Maxwell (117) and on Hg and Sn by Reynolds, Serin & Nesbitt (118). The electronic heat capacities of metals in the superconducting state are discussed by Worley, Zemansky & Boorse (119) and by Maxwell (120). Thermodynamic discussions of the destruction of superconductivity by a magnetic field are given by Garfunkel (121), Pippard (122), and Marcus (123).

*Heat capacities of gases.*—The calorimetric techniques now available permit very accurate measurement of gaseous heat capacities. The isothermal variation of heat capacity with pressure furnishes valuable information on the equation of state and the value of the heat capacity at zero pressure,  $C_p^\circ$ , is a check on the value calculated from molecular data and, in cases where there is uncertainty in vibrational frequency assignment or barriers hindering internal rotation, permits the evaluation of these quantities. Masi & Petkof (124) have measured the heat capacity of  $\text{CO}_2$  and  $\text{O}_2$ . The values extrapolated to zero pressure agreed within 0.1 per cent with values of  $C_p^\circ$ , calculated from spectroscopic data. (An error of 0.2 to 0.3 per cent in the published spectroscopic values of  $C_p^\circ$  was discovered and corrected.) Calorimetric measurements of the heat capacity of  $\text{CO}_2$  up to pressures of

200 atm. and from 20 to 40°C. are reported by Michels & Strijland (125). From measurements on  $\text{CF}_2\text{Cl}_2$  Masi (126) has revised the frequency assignment and recalculated the thermodynamic functions of the ideal gas. He also gives an equation of state consistent with the gaseous heat capacity measurements. McCullough, Pennington & Waddington (127) have measured the heat capacity of water vapor. They use their data to get expressions for the second and third virial coefficients. Barrow (128) has measured vapor heat capacities of  $\text{C}_2\text{H}_5\text{OH}$ . As in the case of  $\text{CH}_3\text{OH}$ , there are serious deviations from ideal gas behavior. Using a frequency assignment based on new infrared measurements, Barrow finds agreement with gaseous heat capacity and third law entropy data with a potential hindering rotation of 3300 cal. for the  $\text{CH}_3$  group and 800 cal. for the OH group. The considerably different assignment of Ito (129) was made without the advantage of the accurate heat capacity data.

#### HEATS AND FREE ENERGIES OF REACTION

*Heats of formation and combustion.*—Calorimetric determinations of heats of formation, based mainly on measurements of heat of combustion are (a) Inorganic compounds: Holley, Huber & Meierkord (130),  $\text{In}_2\text{O}_3$ ; (131),  $\text{ThO}_2$ ,  $\text{UO}_2$ ,  $\text{U}_3\text{O}_8$ ; Huber & Holley (132),  $\text{Nd}_2\text{O}_3$ ; Humphrey & King (133), low-quartz and low-cristobalite; Humphrey, King & Kelley (134),  $\text{FeO}$ ; Koerner & Daniels (135),  $\text{NO}$  and  $\text{P}_2\text{O}_3$ ; Quarterman & Primak (136),  $\text{KC}_4$ . (b) Organic compounds: Nelson & Jessup (137), ethylenimine; Aston, Rock & Isserow (138), methylhydrazine and symmetrical and unsymmetrical dimethylhydrazine; Hubbard *et al.* (139), tropolone (for which the resonance energy is estimated); Cotton & Wilkinson (140), ferrocene; Bender & Farber (141), anthracene transannular peroxide and dianthracene; Carson, Carson & Wilmshurst (142), mercury dimethyl, diethyl, and diphenyl; Mortimer, Pritchard & Skinner (143), various mercury alkyls; Nelson, Jessup & Roberts (144), copolymers of butadiene and styrene; Gilpin and Winkler (145), RDX (trimethylenetrinitramine); Breitenbach, Derkosch & Wessely (146), amino acids and polypeptides. The results of the last-named authors suggest that, in contrast to the first polymers of glycine, the condensation of amino acids to form high molecular weight polypeptides may be exothermic.

*Heats of reaction and of solution.*—Lacher and co-workers (147, 148) have measured calorimetrically the heat of hydrobromination in the vapor phase of butene-1, *cis*-butene-2 and *trans*-butene-2, and the heat of the gaseous reaction  $\text{B}_2\text{H}_6 + 6\text{Cl}_2 = 2\text{BCl}_3 + 6\text{HCl}$ . From the data on the butenes, heats of isomerization are calculated. Jolly & Latimer (149) have measured the heat of the reaction  $\text{GeI}_2(\text{s}) + \text{I}_3^- + 3\text{H}_2\text{O} = \text{H}_2\text{GeO}_3(\text{aq}) + 4\text{H}^+ + 5\text{I}^-$ . Bender & Biermann (150) report heats of neutralization of  $\text{HCl}$  and  $\text{NaOH}$  at high concentrations. From calorimetric determinations of the heat of hydrolysis, Van Artsdalen & Dworkin (151) compute the heat of formation of B-trichloroborazole and in a similar fashion Charnley, Skinner & Smith (152) obtain heats of formation of methyl, ethyl, *n*-propyl, and *n*-butyl esters of



boric acid. Measurements of heats of solution and heats of formation calculated therefrom are: Westrum & Eyring (153), Np in HCl and  $\Delta H_f$  of  $\text{NpCl}_3$  and  $\text{NpCl}_4$ ; Spedding & Miller (154), Ce and Nd and their trichlorides in HCl and  $\Delta H_f$   $\text{CeCl}_3$  and  $\text{NdCl}_3$ ; King (155),  $\Delta H_f$   $\text{MnSiO}_3$  and  $\text{Fe}_2\text{SiO}_4$  from solution in HF; Logan, Bush & Rogers (156),  $\Delta H_f$  of Co (II) and Ni (II) pyridinated cyanates and thiocyanates from solution in HCl; Eyring, Lohr & Cunningham (157), some oxides of Am and Pr in HCl; Evans & Richards (158),  $\Delta H_f$   $\text{GeBr}_4(\text{l})$  and  $\text{GeI}_4(\text{s})$  from solution in NaOH; Li & Gregory (159)  $\text{FeCl}_2$ ,  $\text{FeBr}_2$ ,  $\text{FeBr}_3$ ,  $\text{FeBrCl}_2$  in  $\text{H}_2\text{O}$ . Katzin and co-workers (160, 161) have measured heats of solution of hydrates of uranyl nitrate and of cobalt nitrate in water and a number of organic solvents. From the data they calculate heats of hydration and the binding energies of water and other ligands.

*Free energy and heat data from equilibrium measurements.*—Jolly & Latimer (51, 162) have measured equilibria in the reactions  $2\text{GeI}_2(\text{s}) = \text{Ge}(\text{s}) + \text{GeI}_4(\text{g})$  and  $\text{GeO}_2(\text{s}) + \text{Ge}(\text{s}) = 2\text{GeO}(\text{g})$ . They calculate values of  $\Delta F^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ . Koch, Broido & Cunningham (163) report similar data for the reaction  $\text{LaCl}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) = \text{LaOCl}(\text{s}) + 2\text{HCl}(\text{g})$ . Schäfer and co-workers (46, 47, 48) have investigated equilibria in the reactions  $\text{FeCl}_2(\text{g}) + \text{H}_2 = \text{Fe}(\gamma, \text{s}) + 2\text{HCl}(\text{g})$ ,  $2\text{CoCl}_2(\text{g}) + \text{Cl}_2(\text{g}) = 2\text{CoCl}_3(\text{g})$  and  $2\text{NbCl}_4(\text{s}) = \text{NbCl}_3(\text{s}) + \text{NbCl}_5(\text{g})$ . Chiche (164) has measured equilibrium pressures in the copper-oxygen system and Wunderlich (165) has investigated the thermodynamics of the decomposition of pyrite. Altman & Adelman (166) report measurements on the equilibrium  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}(\text{g}) = \text{N}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$ . The vapor phase association of carboxylic acids has been investigated by Taylor & Bruton (167) and by Lundin, Harris & Nash (168, 169). They find that, contrary to earlier results, the heat of dimerization does not vary much with the nature of the paraffin chain, but there is considerable variation in the entropy change. Doescher (170) and Wise (171) report equilibrium data on the dissociation of  $\text{F}_2$ . Kistiakowsky, Knight & Malin (172) from measurements on detonation velocities of cyanogen-oxygen mixtures, and Thomas, Gaydon & Brewer (173) from flame temperature measurements agree that the dissociation energy of  $\text{N}_2$  is 9.76 e.v.

*Thermodynamic properties from electrochemical cell measurements.*—Values of free energies (and sometimes heats) of formation deduced from electromotive force data are: Suzuki (174, 175),  $\text{AgN}_3$ ,  $\text{TiN}_3$ ,  $\text{TiCN}_3$ ; Koerber & DeVries (176),  $\text{PbF}_2$ ,  $\text{HgF}_2$ , and  $\text{CuF}_2$ . The standard potential of the half-reaction  $\text{GeO}(\text{brown}) + \text{H}_2\text{O} = \text{GeO}_2 + 2\text{H}^+ + 2\text{e}^-$  and the free energy difference of the yellow and brown forms of  $\text{GeO}$  is given by Jolly & Latimer (177). Connick & Hurley (178) give potentials for the couples  $\text{RuO}_4^- - \text{RuO}_4^-$  and  $\text{RuO}_2 \cdot x\text{H}_2\text{O} - \text{RuO}_4^-$ . Jolly (179) summarizes data on ionic heats, free energies, and entropies in liquid ammonia. From cell measurements Nachtrieb & Fryxell (180) show that the anomalous distribution coefficient of  $\text{FeCl}_3$  between aqueous HCl and isopropyl ether is due to an abnormally low activity coefficient of  $\text{FeCl}_3$  in the ether phase.



*Miscellaneous.*—Ramberg (181) reviews the data on heats of formation from the oxides of oxysalts of mineralogical importance and shows the trends with position in the periodic table. Hart (182) examines the periodicity of chemical thermodynamic functions and finds that correlation with position in the periodic table is best shown if values per equivalent (rather than per mole) are used.

#### STATISTICAL CALCULATION OF THERMODYNAMIC PROPERTIES OF GASES

A number of papers has appeared presenting calculations of the thermodynamic functions  $(F^\circ - H_0^\circ)/T$ ,  $(H^\circ - H_0^\circ)$ ,  $S^\circ$  and  $C_p^\circ$ , of ideal gas molecules. Articles in which the calculation is made to the rigid rotator-harmonic oscillator approximation, requiring only a knowledge of the moments of inertia and the fundamental vibration frequencies, are: McDonald (183), OD; Cleveland & Klein (184), O<sub>3</sub>; Stephenson & Jones (185), NOF; Voelz (186), GeF<sub>4</sub>; Voelz, Meister & Cleveland (187), SiF<sub>4</sub> (correction of earlier paper); Davis, Cleveland & Meister (188), CCl<sub>2</sub>Br<sub>2</sub>; Günthard & Kováts (189), CH<sub>3</sub>CN; Ferigle & Weber (190), diacetylene. The calculations of Scheer (191) on ClF<sub>3</sub> are criticised by Weber & Ferigle (192). More refined calculations in which correction is made for anharmonicity of the vibrations and for rotational stretching are given by: Evans & Wagman (193), S, S<sub>2</sub>, SO, SO<sub>2</sub>, SO<sub>3</sub>, H<sub>2</sub>S; Cole, Farber & Elverum (194), F, F<sub>2</sub>, HF; Cole & Elverum (195), ClF, BrF, IF, BrCl, ICl, IBr. In many cases use is made of existing equilibrium or thermal data to choose values of  $\Delta H_0^\circ$  for reactions and the calculated equilibrium constants are tabulated. Waring (196) has reviewed the thermodynamic properties of formic acid. Keller & Johnston (197) calculate an approximate entropy for decaborane. Murphy & Rubin (198) point out that the experimental value for the entropy of F<sub>2</sub> is inconsistent with the spectroscopically calculated one and suggest that there may be an overlooked transition in the solid near 50°K. Other references to statistical calculations of thermodynamic data will be found under Heat Capacities, Heat Contents, and Entropies.

#### HELIUM

The heat capacity of liquid helium has been measured by Hull, Wilkinson & Wilks (199) between 0.6 and 1.6°K. and by Kramers, Wasscher & Gorter (200) between 0.25 and 1.9°K. The data are in substantial agreement. The most interesting result is that below 0.6°K. the heat capacity varies as  $T^3$  and is consistent with that expected from a Debye-like frequency spectrum of longitudinal vibrations only. Above 0.6°K. the heat capacity rises much more rapidly than  $T^3$  because of the still incompletely understood excitation process which culminates in the maximum at the lambda-point. The new low-temperature heat capacity data permit, through the use of the third law of thermodynamics, more accurate calculations of the entropy of liquid helium which are in better agreement with fountain-effect measurements than the old values. Berman & Poulter (201) have measured the volume of

vapor evolved from a calorimeter containing liquid helium when a given amount of electrical energy is introduced. In order to calculate heats of vaporization from their data, it is necessary to know the gas density at the vaporization temperature and the uncertainty in this quantity is the major source of error. An accurate determination of equation of state data on helium gas is badly needed in order to make precise correlation of thermodynamic data on helium. In connection with thermal conductivity measurements Webb, Wilkinson & Wilks (202) have measured the heat capacity of solid helium at three different densities. Because of the large compressibility, there is a considerable decrease of heat capacity with pressure. Swenson (203) has reported data on the solidification curve of helium between 1.6 and 4°K. by a method which involves observation of the isobaric volume change on solidification or melting. He also obtained data for the heat of fusion, which agree well with those calculated from the Clausius-Clapeyron equation using the observed volume changes and values of  $dP/dT$ . If the  $\lambda$  transition from liquid He I to He II is really second order, one may calculate from the Ehrenfest equations relations that must be satisfied among various higher order derivatives at the point where He I, He II, and solid He are in equilibrium. The observed change in the temperature derivative of the volume change on melting agrees with the experimental value, but there is a discrepancy in the change of  $d^2P/dT^2$  along the melting curve. Near the transition, however,  $dP/dT$  is changing rapidly, and it is not sure that the discrepancy is beyond experimental error. The very surprising results on the melting curve of helium reported by Cwilong (204), which were inconsistent with all previous data, were later found by him to be in error.

*Theoretical.*—Ward & Wilks (205) show that second sound and the thermo-mechanical effect in helium at very low temperatures may be understood in terms of elastic collisions between phonons without the need for a two-fluid theory. Kramers (206) discusses the general question of the excitations in the liquid at higher temperatures. A molecular theory of liquid helium based on the cell model of Lennard-Jones and Devonshire is given by Prigogine & Philippot (207). There is an important effect of the nuclear statistics on the calculated properties. Recent review articles on helium are: Atkins (208), *Wave: Propagation and Flow in Liquid Helium II*; Daunt (209), *Properties of Helium Three*; Dingle (210), *Theories of Helium II*.

*Solutions of helium isotopes.*—The spectacular deviations from ideal solution behavior shown by mixtures of helium isotopes three and four has continued to attract investigation. Daunt & Heer (211) report equilibrium liquid-vapor concentrations for a solution about one per cent in He<sup>3</sup>. The quantitative results are uncertain because of difficulties with the mass spectrometer analysis, but qualitatively the results are in agreement with the theory of Heer & Daunt (212). This theory treats the solutions as a statistically independent mixture of Fermi-Dirac (He<sup>3</sup>) and Bose-Einstein (He<sup>4</sup>) ideal gases. The gas molecules are assumed in smoothed potential

wells, and there is assumed to be no volume change on mixing. The parameters are adjusted to fit the properties of  $\text{He}^4$ . The anomalous properties of the solutions arise entirely from the quantum statistics. The theory has been extended by Daunt, Tseng & Heer (213). Sommers (214) reports a careful series of measurements on  $\text{He}^3$ - $\text{He}^4$  solutions at concentrations up to 80 per cent  $\text{He}^3$  in the vapor and at temperatures between 1.30 and 2.18°K. There are significant quantitative deviations from all theories of these solutions that have been advanced. De Boer & Gorter (215) emphasize that there is, in a solution which undergoes a second order transition, a discontinuity in the temperature coefficient of the vapor-liquid concentration ratio at the lambda-point. This was shown in a previous thermodynamic treatment (216) of second order transitions in two-component systems.

*Properties of pure  $\text{He}^3$ .*—Measurements of the melting pressure of  $\text{He}^3$  have been extended down to 0.16°K. by Weinstock, Abraham & Osborne (217). Between 0.5 and 1.5°K. the results may be represented by the equation  $P = 26.8 + 13.1 T^2$  atm. Below 0.5°K. the observed melting pressures vary less rapidly with temperature, but this may be partly because of poor thermal equilibrium between the  $\text{He}^3$  and the paramagnetic salt used. From the Clapeyron equation,  $dP/dT = \Delta S/\Delta V$ , and the melting pressure data one can conclude that, at temperatures of 0.5°K. and higher, the entropy of liquid  $\text{He}^3$  is greater than that of the solid. Since in the solid one would expect the nuclear spin entropy of  $R \ln 2$  to persist to temperatures of 0.01°K. or lower, the conclusion is that at 0.5°K. there is no appreciable nuclear alignment in the liquid. Pomeranchuk (218) predicted that because of the Fermi-Dirac statistics nuclear alignment would occur in the liquid at below about 1°K., and the entropy would become less than  $R \ln 2$ . This would cause the melting pressure to rise at lower temperatures since  $\Delta S$  would change sign. No such effect has been observed. Singwi (219) showed that the vapor pressure data reported by the Argonne workers (220) could be fitted on the assumption that the liquid has the entropy calculated for an ideal Fermi-Dirac gas of mass three and with the density of liquid  $\text{He}^3$ . However, this model would also give a liquid entropy less than  $R \ln 2$  at 0.5°K. and is inconsistent with the melting pressure data. In reviewing the situation, Weinstock, Abraham & Osborne (221) deduce an expression for the entropy of liquid  $\text{He}^3$  consistent with both the vapor pressure and melting data and conclude that in the actual liquid nuclear alignment must occur at an appreciably lower temperature than would be predicted for an ideal Fermi-Dirac gas at the same density.

#### MISCELLANEOUS TOPICS

Mendelssohn (222) has discussed the adiabatic magnetization of superconductors as a method of obtaining temperatures below 1°K. Although the entropy changes are small compared to those of paramagnetic salts, the relatively small magnetic fields required and the fact that the heat capacity of

the normal metal rises with temperature so there is increased thermal stability at higher temperatures may make superconductors preferable for some applications. Schmitt (223) has investigated adiabatic thermal changes in barium titanate ceramic at helium temperatures. The apparent large temperature coefficient of dielectric constant in this ferroelectric material arises from a change in the ease of rotation of domains which is an irreversible process. As in a ferromagnetic substance, there is no appreciable change in entropy upon application of a field and the only thermal effects observed were a result of the irreversible production of heat occurring both upon application and removal of a field. Rothstein (224) discusses the relationship between information as defined in communication theory and entropy. A good earlier treatment of this topic is that of Brillouin (225). A related question is the Gibbs paradox, the classical discontinuity in the entropy of mixing of two gases which are gradually made identical. Landé (226) concludes that from the nonexistence of this discontinuity one can derive the necessity for a quantum theory, although not, of course, the value of Planck's constant.

*Thermodynamics of irreversible processes.*—There is continued interest in the theory of steady state processes in which some inherently irreversible process is taking place. In many cases the logically more satisfying treatment based on the Onsager reciprocity relations leads to the same result as the classical treatment in which the irreversible part of the process was ignored. Examples are the Kelvin treatment of electromotive force and London's derivation of the fountain-effect equation in helium. In some cases, however, new relationships are predicted, and it is hoped that the theoretical work will stimulate experiments in this field. Papers appearing in 1952 are: Callen (227), thermomagnetic effects; Callen & Greene (228), a generalization of the Nyquist electrical noise formula; Tolhoek & de Groot (229), the first law of thermodynamics in systems with flow of matter across the boundaries; Denbigh (230), heat of transport in binary regular solutions; Staverman (231), membrane processes; Tyrrell & Hollis (232), thermal diffusion potentials in nonisothermal electrolytic systems; Davies (233), the Joule-Kelvin effect. Unlike other workers, Verschaffelt (234, 235) does not use the Onsager relations, but employs a principle of superposition in discussing transport phenomena. His treatment is criticized by Overbeek & Mazur (236) and by Davies (237).

*New methods and apparatus.*—Borovik-Romanov & Strelkov (238) describe a new gas thermometer in which a pressure-sensitive diaphragm is used to minimize the dead space volume. They report measurements of the boiling points of normal and of equilibrium hydrogen. Michels, Wassenaar & Zwietering (239) describe an apparatus for measuring PVT data of gases which uses a diaphragm sensitive to one thousandth atmosphere. In measurements on dry air, a consistency of one part in a hundred thousand was obtained. Clement & Quinnell (240) and Geballe *et al.* (241) have investigated

carbon resistance thermometers for use at low temperatures. The latter investigators studied the effect of particle size and of gas adsorption. Giauque *et al.* (242) report data on the properties of a methyl methacrylate plastic (Plexiglas) for use in calorimetric and magnetic investigations at very low temperatures.

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# HETEROGENEOUS EQUILIBRIA AND PHASE DIAGRAMS<sup>1</sup>

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The subject of heterogeneous equilibria is a vast one embracing many fields. Even in only one year, so much work is done which touches on this subject that in attempting a review the authors can only hope to mention briefly a few of those studies which seem most outstanding or those which appear to be most nearly representative of the work in each major field.

Based on their chemical compositions, heterogeneous systems may be divided into the broad categories of (a) aqueous-salt systems, (b) organic systems, (c) salt systems, (d) metallic systems, and (e) oxide, carbide and nitride systems. In general, the temperature range of interest and the difficulty of investigation increase in the order in which these categories are listed. Inasmuch as relatively few anhydrous salt systems have been reported during the year, items (a) and (c) will be discussed in a single section.

Each year new types of equipment are designed and new techniques are developed for investigating the phenomena of phase equilibria. The challenge exists principally in the fields most difficult to study, i.e., in those systems in which a liquid phase is formed only at elevated temperatures or in those which require study at pressures considerably above one atmosphere. The majority of developments both in equipment and technique are therefore concerned with alleviating difficulties normally encountered in the investigation of these two types of systems. Because of the importance of innovations in equipment and technique to future studies of heterogeneous equilibria, some of the latest developments along these lines are first discussed under a separate heading.

## EQUIPMENT AND EXPERIMENTAL TECHNIQUES

Christensen & Roedder (1) have discussed in considerable detail the experimental techniques employed in phase equilibrium studies of systems at elevated temperatures. During the past year, however, there have been a number of advancements made in both equipment and technique which are worthy of mention.

The method of differential thermal analysis (DTA) has continued to be used extensively during this period, particularly in the studies of clays, carbonates, and hydrates. DTA has been found especially valuable in studies of the transformations of the clay minerals. The thermal transformations of kaolinite, for example, cannot be followed by x-rays because of the appar-

<sup>1</sup> The survey of the literature pertaining to this review was concluded in January, 1953.

ently amorphous phase that occurs between 550° and 950°C. [Brindley (2)]. X-ray studies of fine-grained clays are limited to the powder method which is inadequate for detailed investigations. Single-crystal studies are therefore generally made of the larger-grained polymorphs such as nacrite (a kaolinite polymorph). These results are considered as probably valid also for the fine-grained clay minerals. DTA equipment developed by Stone (3) is especially well suited to clay studies. He has designed an apparatus for carrying out the differential thermal analysis of a powdered sample under controlled partial pressure of water, carbon dioxide, or other gases.

Haul & Heystek (4) used DTA to study the decomposition of dolomite under various CO<sub>2</sub> pressures. Barshad (5) has described how DTA equipment can be calibrated for obtaining temperatures and heats of reaction. The method consists of obtaining DTA curves of organic and inorganic substances of known melting or inversion points and of known heats of fusion and heats of decomposition. The initial point of the differential break marks the temperature of beginning of fusion while the area under the differential curve is proportional to the heat of fusion. The materials selected for calibration are those which give an abrupt break in the  $\Delta T$  curve. Kiyoura & Sata (6) have employed similar methods for the studies of carbonate and hydroxyl systems. They measured the area under the peak produced by the decomposition of calcium carbonate with a planimeter to determine the percentage of calcium carbonate present. A linear relationship was found between this area and the quantity of calcium carbonate in the sample. The accuracy of the determinations was plus or minus 2 per cent.

The method of thermal analysis has always been employed extensively in the study of metal systems. At low temperatures, however, the sensitivity of the method is not generally very great. Recently, a sensitive method for the thermal analysis of very low melting alloys was developed [Evans, Fromm & Jaffee (7)]. The method is suitable for work in the temperature range -72° to +230°C.

As a further aid to the study of the thermal decomposition of carbonates, sulfates, hydrates, etc., Mauer (8) has developed an improved recording analytical balance which maintains a continuous record of changes in weight of a specimen during heating. The balance is capable of following very rapid changes in weight without oscillating and with an accuracy better than 0.5 per cent of the total change involved. As a further step, Mauer has combined the recording balance with a differential thermal analysis apparatus so that both the changes in weight of the material and the DTA curve are recorded simultaneously on the same chart while two specimens of the material are being heated in the same furnace under nearly identical conditions. Two separate samples are employed because of the difficulty in recording sensitive weight changes of a sample having thermocouples attached to it. With this equipment one not only obtains information in the form of a record of changes in weight of a specimen during heating, but also has a means of interpreting the result of the differential thermal analysis.

In studies of the salt-water systems and of many of the organic systems, it is quite common for the investigator to take a sample of the liquid phase for chemical analysis after equilibrium has been established. This procedure has rarely been resorted to in the study of high temperature phase equilibria, however, because of difficulties involved in securing a sample of the pure liquid. Newkirk & Ordway (9, 10) have developed a high-temperature centrifuge with which it is possible to secure a sample of the liquid phase in certain inorganic systems at temperatures up to 1600°C.

The use of measurements of heat effects, volume changes, changes in optical properties, etc., to study the occurrence of structural or phase changes is well known. Other phenomena may also be profitably employed to determine these changes. For example, in studies of  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  mixtures freezing at 1266°, Ford & White (11) measured the change of electrical resistance and capacitance of the mixtures with temperature up to the liquidus temperature. In the solid state (up to about 1200°) the temperature-resistance relations conform to the usual expression  $R = ae^{E/RT}$ . Above 1200° a phenomenon known as premelting occurs. Over this range the slope of the resistance curve increases progressively until the solidus temperature is reached. The premelting region is also characterized by a corresponding rise of capacity of the mixture. At the solidus temperature an abrupt change in the slope of the temperature-resistance or temperature-capacity curve occurs. As the temperature continues to rise with further increase in the liquid content, the rates of change of resistance and capacity with temperature undergo a progressive reduction. In certain cases there is also an additional break in the curve at the liquidus temperature.

For a number of years microradiography has been employed to study the phases occurring in metallic systems. In preparing microradiographs, an x-ray beam is passed through a very thin slice of the specimen and registers as a small black dot on a film placed just behind the specimen. The film used is very fine-grained so that the resulting image can be subjected to a magnification of 100–200 $\times$ . Advantage is taken of the difference in absorbing power of the different elements at the selected wavelength of the beam. By judiciously selecting the wavelength it is therefore possible in some systems to make one phase stand out in the microradiographs so as to be distinguishable from the others. The method is of value only when there is a sufficient difference in absorption between two phases at the selected wavelength. There is no reason why the method cannot be employed advantageously in the study of certain mineralogical and ceramic oxide systems. Epprecht (12) has recently discussed the applicability of microradiography to petrography and mineralogy.

In studying melting relations, many investigators have in the past utilized some form of high-temperature microscope to observe the beginning or end of melting. The method continues to be popular in present-day phase equilibrium work. The heating units used with the microscope range from rather large furnaces utilizing special lenses to permit microscopic observa-

tions at some distance [Bauman (13)] to very small wire filaments or strips on which the sample is placed [Roberts & Morey (14)].

Various refinements in the earlier techniques have appeared from time to time. For example, Carter & Ibrahim (15) employed a modification of the high-temperature microscope developed by White, Howat & Hay (16) in a study of the ternary system  $\text{Na}_2\text{O}-\text{FeO}-\text{SiO}_2$  while Hill, Roy & Osborn (17) used a small strip furnace somewhat similar to the "Meldometer" of Joly (18) in their investigation of the gallia-alumina system. Ordway (19) has developed a hot-wire apparatus for growing crystals from refractory melts and for preliminary phase equilibrium observations. With his apparatus a single filament acts as both the heating element and the thermocouple for measuring the temperature of the small charge. The charge is placed at the junction of a platinum-10 per cent rhodium thermocouple, and observed under a binocular microscope. The filament is heated by means of an audio frequency current. The audio frequency signal is removed by a filter section and the emf. produced by the thermocouple is measured to determine the temperature of the sample at the junction. The temperature at which a phase change is seen to occur under the microscope is thus readily determined. In a more recent improvement of the apparatus, Ordway (20) has added a controller for maintaining the tiny charge at any selected temperature.

The investigation of phase equilibria in systems at elevated temperatures and water pressures requires, for accurate work, the use of a high-pressure pumping system to maintain the bombs at a known constant pressure. At pressures of the order of 30,000 psi most pumps tend to wear rapidly so that frequent repairs are necessary. A simple and economical device developed by Roy & Osborn (21) makes use of a commercial jack to obtain the desired pressure and offers promise in overcoming many of the previous difficulties. The apparatus consists essentially of a stainless steel chamber in which water is compressed by the jack. Pressures as great as 200,000 psi are said to be obtainable with this equipment if valves are eliminated from the system. With valves present, a large number of bombs can be operated from the same compressor and pressures approaching 60,000 psi can be maintained.

In order to accelerate hydrothermal reactions Roy and Osborn added stainless steel rods to charges held in Morey-type bombs and rotated the bombs at 20 rpm. while maintaining them at the desired temperature and pressure. Using this grinding technique, they were able to decompose andalusite, sillimanite or kyanite to form kaolinite detectable in x-ray diffraction patterns within 3 days while under the same conditions of temperature and pressure, but without the grinding treatment a period of three months was insufficient to produce enough kaolinite to give a diffraction pattern.

An improved apparatus for determining the solubility of salts and minerals in superheated steam at high pressures was described by Morey &



Hesseltger (22). With the new apparatus, pressure control is maintained by a Baldwin Hood pressure cell, the sensitive elements of which are two Baldwin strain gages which are used in conjunction with a Brown electronic potentiometer. The improved instrument has a pressure range up to 49,500 psi and a high sensitivity.

#### SALT AND AQUEOUS SALT SYSTEMS

Some of the earliest work involving the application of the phase rule to practical problems consisted of the study of salt and aqueous salt systems. Systems of this type do not generally present serious difficulties in their investigation, since the experiments are ordinarily carried out at atmospheric pressure and at temperatures readily obtainable in the laboratory. With the development of improved laboratory equipment and techniques, attention has gradually drawn away from these systems and has focussed instead on the investigation of other types of systems previously neglected because of what then appeared to be insurmountable experimental difficulties. Nevertheless, new material in this field has certainly not been exhausted, and a few salt systems and a relatively large number of salt-water systems (usually isothermal sections) continue to be reported each year.

In general, the methods commonly employed to determine phase relations in anhydrous systems of one or more salts are essentially identical to those used to study the more refractory mineralogical and ceramic systems. These consist principally of various modifications of heating and cooling curve methods (either direct or differential thermal analysis), microscopic examination of heat-treated samples and x-ray diffraction measurements during or after heat treatment. With aqueous salt systems the procedure is somewhat different and may be illustrated by a brief description of the method used by Ricci & Selikson (23) in determining solubility isotherms in ternary aqueous systems containing a sulfamate and the corresponding halide. Complexes of known composition were placed in glass tubes containing marbles to provide agitation and were rotated in constant-temperature water baths. After sufficient time had elapsed for the attainment of equilibrium, the solutions were sampled through filter paper into pipettes and the saturated solution subjected to chemical analysis. The composition of the solid phase in each sample was then calculated by algebraic extrapolation of tie-lines fixed by the compositions of the total complex and the liquid solution. For a few samples, Schreinemakers' method of "wet residues" was employed (24). This method consists of establishing a tie-line by analyzing the saturated solution and also a sample of the solid phase still wet with the mother liquid.

By the methods described above, Ricci and Selikson determined that at 25°C. the following appeared as simple ternary systems with only the pure salts as solid phases: ammonium sulfamate-ammonium chloride-water; potassium sulfamate-potassium chloride-water; potassium sulfamate-potas-

sium iodide-water; potassium sulfamate-potassium sulfate-water; ammonium sulfamate-ammonium sulfate-water.

The aqueous system of ammonium and potassium sulfamates, however, at 9°, 25° and 45°C. form extensive solid solutions with a miscibility gap. Distribution relations are of the Roozeboom Type V [see Ricci (25)]. The 25° isotherm of the reciprocal quaternary system water and the salt pair ammonium sulfamate-potassium sulfate showed only three solid phases: a continuous series of solid solutions of the sulfates and two series of solid solutions of the sulfamates.

Studies of the reciprocal system  $\text{RbCl} + \text{KBr} = \text{RbBr} + \text{KCl}$  indicate that for each mixture in the system a solid solution is formed which contains all four of the ions [Wood & Breithaupt (26)]. A system of this type is ternary since any one of the four compounds may be represented by a combination (either positive or negative) of the other three. For other systems involving bromine, simple eutectics were found for aluminum bromide-bromine, bromoform-aluminum bromide, and bromobenzene-aluminum bromide. A 1:1 complex is formed between pure ethyl bromide and aluminum bromide [Burbage & Garret (27)]. Cadmium bromide-zinc bromide and cadmium bromide-lead bromide also form simple eutectic systems. In the system cadmium bromide-silver bromide, however, there is evidence of compound formation in the region 70–80 per cent silver bromide [Zakharchenko (28)].

From an examination of phase relations in the system sodium bromide-sodium chloride –6.6 molar sodium hydroxide at 35°C., Simons, Orlick & Vaughan (29) obtained evidence that the two salts form a continuous series of solid solutions. This experimental result is not in agreement with calculations of others who predicted limited miscibility below 50°C. in the binary system.

In simple salt-water systems equilibrium may be reached within a period of from a few hours to a few days. With the formation of complex double salts, however, a system may require several weeks of stirring at constant temperature to attain equilibrium. This was true, for example, for the systems  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{Ba}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  and  $\text{BaBr}_2 \cdot \text{Ba}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  investigated by Ricci & Freedman (30). These nitrate systems form incongruently soluble hydrated double salts tentatively identified as  $(\text{Ba}(\text{ClO}_3)_2 \cdot 6\text{Ba}(\text{NO}_3)_2 \cdot 12\text{H}_2\text{O})$  and  $\text{BaBr}_2 \cdot 8\text{Ba}(\text{NO}_3)_2 \cdot 12\text{H}_2\text{O}$ . The double salts are stable at 10° and 25° but not at 45°C. In further work on aqueous systems involving barium halates, Ricci & Freedman (31) determined that the incongruently soluble double salt  $\text{Ba}(\text{BrO}_3)_2 \cdot \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  appears in the system  $\text{Ba}(\text{BrO}_3)_2 \cdot \text{BaCl}_2 \cdot \text{H}_2\text{O}$  at 10°, 25°, and 45°C., the range of stability increasing slightly with rising temperature. The same investigators discovered an incongruently soluble anhydrous compound  $\text{Ba}(\text{IO}_3)_2 \cdot \text{I}_2\text{O}_5$  in the system  $\text{Ba}(\text{IO}_3)_2 \cdot \text{I}_2\text{O}_5 \cdot \text{H}_2\text{O}$ .

Aqueous and nonaqueous systems composed of the chlorides and sulfates of sodium, potassium, magnesium and calcium have been under extensive

study for years due to the fact that these are the principal constituents of sea water and of Central European salt deposits. Feakes (32) studied part of the system potassium-magnesium-sodium-sulfate-chloride-water at 90°C. because of the relationship of this system to the development of a process for the recovery of potassium and other salts from alunite. He found that vanthoffite ( $3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$ ) and langbeinite ( $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ ) may coexist at 90°. There is also some evidence that under certain conditions magnesium sulfate may form a solid solution with sodium sulfate.

Isothermal studies of three aqueous ternary systems with ammonium sulfate as a second component and the sulfate of caesium, potassium, or rubidium as the third were made by Calvo & Simons (33). For the rubidium system, the 35°C. isotherm was determined while for the other two, the 25° isotherm. All three systems show continuous solid solution. The caesium system is of the Roozeboom Type II. The other two are of the Roozeboom Type I.

Argentous and thallous salts usually exhibit a marked similarity in chemical properties. On the other hand, Ricci & Fischer (34) found that continuous solid solutions exist between thallous sulfate and both ammonium and potassium sulfates even though argentous sulfate does not form solid solutions with either of these salts. In the aqueous ternary system containing thallous and copper sulfates, a hydrated double salt  $\text{Tl}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$  isomorphous with the corresponding double salts  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{K}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ , exists.

The eutectic in the system cryolite-sodium fluoride is an excellent solvent for oxides such as  $\text{La}_2\text{O}_3$ ,  $\text{ThO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{CaO}$ , and  $\text{B}_2\text{O}_3$  according to Petit (35). The solution of oxides in molten cryolite was also investigated by Hayakawa & Kido (36) who determined the solubility of magnesia and lime in the molten salt. In the system  $\text{Na}_6\text{CaSiO}_4\text{-CaF}_2$ , a compound  $\text{Ca}_2\text{SiO}_4 \cdot 2\text{NaF}$  is formed which melts incongruently at about 900°C. A simple eutectic appears with this compound and  $\text{CaF}_2$  [Brisi (37)]. Matthias (38) found that a phase transition of the order-disorder type occurs in ( $\text{ND}_4$ )  $\text{D}_2\text{PO}_4$  at 242°K.

Liquid-solid equilibria in the anhydrous quaternary system containing  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ ,  $\text{NaF}$ ,  $\text{KF}$ , and  $\text{CaF}_2$  were the subject of a study by Ishaque (39). Twelve solid phases occur in the system including the six simple salts; three double salts,  $2\text{KCl} \cdot 3\text{CaCl}_2$ ,  $\text{CaCl}_2 \cdot \text{CaF}_2$ , and  $\text{KF} \cdot \text{CaF}_2$ ; a series of continuous solid solutions in the system sodium chloride-potassium chloride and two series of solid solutions with a miscibility gap in the system sodium fluoride-potassium fluoride.

The ternary system cuprous chloride-cupric chloride-potassium chloride is characterized by the lack of significant solid solution and a low liquidus temperature throughout relatively a large portion of the system. This is due to the formation of the relatively low melting compounds  $\text{KCu}_2\text{Cl}_3$ ,  $\text{K}_2\text{CuCl}_4$ , and  $\text{K}_2\text{CuCl}_3$  in this system [Fontana *et al.* (40)].

The behavior of ferrous chloride in concentrated HCl solution resembles more closely that of nickel chloride than of cobalt chloride even though iron is adjacent to cobalt in the Periodic System [Schimmel (41)]. The isothermal study of the system ferrous chloride-ferric chloride-water at 25°C shows that it is not possible to prepare mixed chlorides of iron by concentrating aqueous solutions containing both salts.

The system phosphorus pentoxide-calcium chloride and phosphorus pentoxide-fluorapatite was the subject of a study by Montel (42).

#### ORGANIC SYSTEMS

In many industrial chemical processes, undesirable secondary reaction products are formed which must be removed from the system. In some instances this removal can be effected by using selective solvents to dissolve the impurities. In certain hydrocarbon oxidation processes, for example, the products derived from the reactions contain alcohols and acids. The removal of these impurities has constituted a problem to the industry. In attempting to develop a suitable solvent for removing acetic acid and ethyl alcohol from aqueous solutions, Oualline & Van Winkle (43) studied the two ternary systems 3 heptanol-water-acetic acid and 3 heptanol-water-ethyl alcohol at 25°C. They concluded that 3-heptanol could be used industrially as a solvent for the extraction of ethyl alcohol or acetic acid from aqueous solutions if a suitable means could be found to recover the solvent. The principal difficulty lies in the fact that for acetic acid at the temperature of rectification, esterification may occur.

The effective removal of acetic acid from water solutions was also the object of a study by Sohoni & Warhadpande (44) of the system ethyl acetate-acetic acid-water at 30°C. The plait point for this system (at 30°C.) was located at 22.0 per cent acetic acid, 45.3 per cent water, and 32.7 per cent ethyl acetate. These investigators found ethyl acetate to be superior to three other solvents studied, namely, isopropyl ether,  $(C_2H_5)_2O$ , and creosote, in that less ethyl acetate was required to make the separation.

A considerable amount of work has been reported during the past year on organo-water systems. The system water-biuret was investigated at atmospheric and higher pressures by Rollet & Cohen-Adad (45). A solid phase corresponding to a molar ratio of 5 biuret to 4 water was obtained by recrystallization from an aqueous solution. A eutectic at which ice and biuret hydrate are in equilibrium with liquid was located at 0°C. in the composition range 0.084 to 0.48 per cent biuret.

In the field of biochemistry, x-ray diffraction studies of aqueous systems of the sodium salt of desoxyribonucleic acid were made by Riley & Oster (46).

Phase equilibria in the systems methane-water and ethane-water were studied at selected temperatures up to 340°F. and at 18 different pressures between 200 and 10,000 psi, by Culberson & McKetta (47) while those of

the system propylene oxide-water were investigated at atmospheric pressure by Wickert, Tamplin & Shank (48). Templeton & Daly (49) found evidence of the separation of what may be a tetrahydrate of  $\text{Ni}(\text{NO}_3)_2$  in the alcohol-rich region of the system nickel (ous) nitrate-hexyl alcohol-water at 25°C. The portion of the phase diagram in the water-rich region, i.e., below the  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  phase boundary was developed in detail.

A discussion of vapor-liquid equilibria in hydrocarbon-water systems was given by Kobayashi (50). Organick & Brown (51) derived empirical relations and tables for use in predicting hydrocarbon vapor-liquid equilibria while Winn (52) went a step farther in industrial application and developed a simplified nomographic method for obtaining similar data. Benedict *et al.* (53) also developed a graphic method and published a set of charts for predicting liquid-vapor equilibria as did Rzaa, Glass & Opfell (54).

Whipple (55) recently completed a study of the vapor-liquid equilibria of five binary highly fluorinated systems. The systems studied included:  $\text{CF}_2\text{HCl}-\text{CF}_2\text{Cl}_2$ ,  $\text{CF}_2\text{HCl}-\text{CF}_2$ ,  $\text{CFCF}_3$ ,  $\text{CF}_2\text{HCl}$ -cyclic  $\text{C}_4\text{F}_8$ ,  $\text{CF}_2\text{Cl}_2$ - $\text{CF}_2$ ,  $\text{CFCF}_3$ , and  $\text{CF}_2\text{Cl}_2$ -cyclic  $\text{C}_4\text{F}_8$ . Azeotropes were found to exist between  $\text{CF}_2\text{HCl}$  and  $\text{CF}_2$ ,  $\text{CFCF}_3$  and between  $\text{CF}_2\text{Cl}_2$  and  $\text{CF}_2$ ,  $\text{CFCF}_3$ . Whipple's work constitutes what is apparently the first published data on vapor-liquid equilibria for highly fluorinated systems.

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Phase transitions in sodium and potassium salts of higher fatty acids were the subject of a study of Ravich & Nochitallo (57) who employed the method of differential thermal analysis to determine transition temperatures. The conditions under which the freshly-prepared soaps were dried affected the DTA curves below 70°C. For potassium soaps, increasing molecular weight caused a shift in the phase transition temperatures, while for the sodium soaps this shift did not occur. Anhydrous sodium soaps were found to have lower melting points than the corresponding potassium soaps. Sodium and potassium salts of the same fatty acid differ in both the number and temperature of phase transitions.

Binary freezing-point diagrams were obtained by Mod & Skau (58) for the stable and metastable forms of acetamide with elaidic acid and with the stable and metastable forms of oleic acid. It was determined that acetamide forms a molecular compound with both elaidic and oleic acids. Each of the compounds exhibits two incongruent melting points, one stable and the other metastable.

#### OXIDE, CARBIDE AND NITRIDE SYSTEMS

The study of silica systems containing FeO is of considerable importance

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#### OXIDE, CARBIDE AND NITRIDE SYSTEMS

The study of silica systems containing  $\text{FeO}$  is of considerable importance



to the fields of petrology, metallurgy, and ceramics. For example, a progression of studies leading to the investigation of the quinary system  $K_2O \cdot FeO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$  should yield, among other minerals, the iron analogue of biotite [Roedder (59)]. This information in conjunction with data on the system  $K_2O \cdot MgO \cdot Al_2O_3 \cdot SiO_2$  (currently being studied by Schairer) should be of value in interpreting the stability relationships of most of the natural biotites and of many of the associated hydrous and anhydrous minerals.

The investigation of systems containing FeO requires the use of special experimental techniques in order to maintain the iron in the ferrous state. The pioneering work in developing techniques for studying phase equilibria in FeO-SiO<sub>2</sub> systems was carried out by Bowen & Schairer (60) in 1932. In studying phase relationships by the quenching method, the small charges are ordinarily enclosed in platinum envelopes or placed in open platinum pans [Swayze (61)] which are suspended in the furnace. Mixtures in the ferrous-iron systems, however, are placed in pure metallic iron crucibles [Muan & Osborn (62)] or in envelopes made from iron foil of high purity [Roedder (59)] for heat treatment.

In addition, in preparing the batch of each composition, iron lathe chips are added to the mixture and final treatments are carried out in an oxygen-free atmosphere. The FeO content of each mixture must be determined by a chemical analysis of the mixture after the preparatory heat treatments. The proportions of the other components are fixed by synthesis. In spite of all precautions, however, part of the iron is always present as Fe<sub>2</sub>O<sub>3</sub>, and this must always be determined and accounted for. In preliminary work on the system  $K_2O \cdot 2SiO_2 \cdot FeO \cdot SiO_2$ , for example, Roedder found from 0 to 6 per cent of Fe<sub>2</sub>O<sub>3</sub> in samples quenched from their individual liquidus temperatures. The quantity present depended for the most part on the total iron content of the mixture. The system investigated is thus actually quaternary in nature although for most practical purposes it may be considered as ternary.

Muan and Osborn are carrying out an extensive series of phase-equilibrium investigations of systems involved in steel plant refractory problems. Of particular concern are those systems which involve the constituents of steel plant refractories and the slags which attack them. The system  $CaO \cdot FeO \cdot Al_2O_3 \cdot SiO_2$  is of importance in this respect. Previous studies by Schairer (63) describe phase equilibria in the high silica part of the system for compositions higher in silica than the join  $CaO \cdot SiO_2 \cdot 2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot FeO$ . Muan and Osborn have extended this earlier work to lower silica compositions by investigating the system  $2CaO \cdot SiO_2 \cdot CaO \cdot SiO_2 \cdot 2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot FeO$ . They found that a liquid phase appeared in certain mixtures in this system below 1200°C. This accounts for the poor resistance of aluminosilicate refractories to attack by lime-iron silicate slags, while, on the other hand, the low liquidus temperatures makes the use of such



slags feasible. Three quaternary invariant points at which four crystalline phases coexist in equilibrium with liquid were located in this system. All of these invariant points were found to have similar liquidus temperatures and alumina content (about 5 per cent). Within the tetrahedron representing the four-component system, melilite crystals encountered were solid solutions of the composition  $\text{Ca}_2(\text{Al}, \text{Fe})(\text{Al}, \text{Si})\text{SiO}_7$ . X-ray diffraction data were obtained which can serve in the identification of members of the solid-solution series in the system  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ - $2\text{CaO} \cdot \text{FeO} \cdot 2\text{SiO}_2$ . As Fe plus Si substitutes in the structure for 2Al, the unit cell changes in shape by an increase in *A* and a decrease in *C*.

As a result of their study of the system  $\text{Na}_2\text{O}-\text{FeO}-\text{SiO}_2$ , Carter & Ibrahim (15) report the existence of a ternary compound having the formula  $\text{Na}_2\text{O} \cdot \text{FeO} \cdot \text{SiO}_2$ . The compound melts incongruently at 976°C. to form wustite (FeO) plus liquid. Another ferrous system,  $\text{Fe}-\text{FeS}-\text{FeO}-\text{SiO}_2$ , is characterized by the presence of regions of two or three liquid phases [Ol'Shanskii (64)]. In the presence of FeS, fayalite ( $2\text{FeO} \cdot \text{SiO}_2$ ) decomposes on melting into  $\text{SiO}_2$  plus liquid rather than forming the normal products, Fe plus liquid. Replacement of part of the fayalite by dicalcium silicate strongly reduces the solubility of FeS in the melt [Ol'Shanskii (65)].

In a recent study of the system  $\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ , it was concluded that diasporé ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) forms in nature only at temperatures above about 275°C. and at pressures exceeding 2000 psi [Erwin & Osborn (66)]. The location of the boehmite ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ )-diasporé transformation curve was established only by approach from the low-temperature side since diasporé, once formed, could not be made to invert to boehmite. It was thought that by substituting  $\text{Ga}^{3+}$  for part of the  $\text{Al}^{3+}$  in the structure, diasporé might be more prone to transform to boehmite under pressure-temperature conditions in which the latter form is stable [Hill, Roy & Osborn (17)]. The ion  $\text{Ga}^{3+}$  has properties very similar to those of  $\text{Al}^{3+}$  so that an isomorphous substitution of one ion for the other is quite common throughout the rock series. Roy, Hill & Osborn (67) made a study of the system gallia-water over the pressure range 50 to 25,000 psi at temperatures up to 800°. The equilibrium diagram has only two fields, those for  $\beta\text{-Ga}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (gallian diasporé), separated by a univariant line at  $300 \pm 5^\circ\text{C}$ . No gallia hydrate structure corresponding to boehmite is known. In the system alumina-gallia-water, Hill, Roy & Osborn (17) found a complete series of diasporé solid solutions extending from  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  to  $\text{Ga}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . Boehmite solid solutions extend to approximately the composition  $70\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ,  $30\text{Ga}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . In the anhydrous system, at high temperatures extensive solid solution characterizes the  $\alpha\text{-Al}_2\text{O}_3$  and  $\beta\text{-Ga}_2\text{O}_3$  structures. Below 810°C. a compound  $\text{GaAlO}_3$  and a new series of alumina-gallia structures are stable. The results of the study of the ternary system are consistent with the thesis that diasporé ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) is stable only above about 275°C.

The system alumina-silica-water is characterized by a large number of

crystalline phases (at least 20 have been identified), many of which are common minerals [Roy & Osborn (68)]. The compound  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  exists as four different structural modifications: kaolinite, nacrite, dickite, and halloysite. Other ternary compounds in the system include endellite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ ) and pyrophyllite ( $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ ). In addition, two new ternary compounds have been discovered by Roy and Osborn. One of these has a structure resembling that of montmorillonite and may correspond to the pure alumina end of the beidellite series. The composition and structure of the other ternary compound is not definitely established, but the composition is believed to approximate  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ .

A crystalline phase essentially identical with natural sapphirine was discovered by Foster (69) in solid-phase studies in the high-alumina portion of the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ . On the basis of Foster's discovery, Keith & Schairer (70) re-examined a portion of the ternary system and located a tiny stability field of sapphirine. This field is bounded by the spinel, cordierite, and mullite primary-phase regions. Three ternary invariant points, not eutectics, were located. The temperature range over which sapphirine crystals appear in equilibrium with liquid is very short ( $1453^\circ$  to  $1482^\circ\text{C}$ ). Conclusive evidence of the chemical composition of synthetic sapphirine has not been obtained, but Keith and Schairer agree that the composition deduced by Foster ( $4\text{MgO} \cdot 5\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) is the most probable one.

The compound  $\text{MgSiO}_3$  is known to undergo polymorphic transition. There is considerable disagreement, however, among the various investigators as to the number and structures of the stable forms of this compound. As a result of a re-examination of solid phase equilibria in the system  $\text{MgSiO}_3\text{-CaMgSi}_2\text{O}_6$ , Atlas (71) has concluded that there are only two stable forms of  $\text{MgSiO}_3$ , orthorhombic enstatite up to about  $985^\circ\text{C}$ . and protoenstatite from  $985^\circ$  to the dissociation point. Clinoenstatite, although it occurs in nature, was found to be only a metastable low-temperature phase formed during rapid cooling of protoenstatite. In the binary system, however, a clinoenstatite solid solution may exist as a stable phase.

Eitel (72) has stressed the importance of solid-state reaction to the synthesis of fluorosilicates of the mica and amphibole group, while Barrer (73) has reviewed the aluminum silicate minerals which have been synthesized in his laboratory. While many species synthetically crystallized are essentially identical with their natural occurring counterparts, others, although having related structures, differ characteristically in some properties from the corresponding natural species. A number of related compounds have also been produced of which natural counterparts have never been reported [Barrer & White (74)].

The system diopside ( $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ )—forsterite ( $2\text{MgO} \cdot \text{SiO}_2$ )—anorthite ( $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) is an important one geologically because it represents three mineral groups, the pyroxenes, olivines and feldspars, which are quantitatively the major silicate structures composing the earth's crust.

The system has recently been reported by Osborn & Tait (75) who investigated it as part of the quaternary system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  on which work is in progress. Owing to the fundamental difference in type of structure of the three compounds, virtually no solid solution or reaction relation exists among the phases in the ternary system. An invariant point tentatively classed as a eutectic occurs at 1270°C. at which diopside, forsterite, and anorthite are in equilibrium with a liquid of the composition (weight per cent) 7.5 forsterite, 49 diopside and 43.5 anorthite. A field of spinel also appears in the system between forsterite and anorthite above 1317°.

Rosenqvist (76) reported studies of the reactivity of alkali feldspars in the solid state. Abnormally high as well as abnormally low reactivity was found at different temperatures. These results were attributed to transitions between different modifications.

Petrologists generally consider that water is of importance to many later stage igneous processes as well as to metamorphism and weathering. It is also generally accepted that in the presence of water, the stability of the plagioclases decreases with increasing anorthite ( $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) at low temperatures [Graham (77)]. Under these conditions the soda-rich (albitic) plagioclase persists while the lime-rich (anorthitic) feldspar is decomposed. Of the minerals generally considered to be formed in place of the calcic plagioclases, the nearest in chemical composition to anorthite are zoisite ( $3(\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) \cdot \text{Ca}(\text{OH})_2$ ) and lawsonite ( $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ). In certain instances each of these minerals has been found in nature as a product of plagioclase hydration and breakdown. As the first step to the experimental evaluation of hydrothermal stability relations of the plagioclases, Goldsmith & Ehlers (78) studied the system anorthite-water at temperatures up to 500°C. and pressures up to 15,000 psi. Their results are contrary to the hypothetical equilibrium diagram postulated by Ramberg (79). Neither zoisite nor lawsonite was produced in any of the experiments. Anorthite was observed to be stable in the presence of water at temperatures down to 350°C. and possibly somewhat lower. A hexagonal polymorph of anorthite which may be the stable form below 300°C., occurred together with anorthite in the range 300–375°C., the hexagonal modification being less evident at the higher temperature. This hexagonal form has not been observed in nature. The attainment of equilibrium below 300°C. necessitates experiments of extremely long duration. It is thus possible that the hexagonal form may be metastable, and that experiments of greater duration may produce one of the naturally occurring phases.

In further studies of the solubilities of minerals in superheated steam at high pressures, Morey & Hesselgesser (22) determined the solubilities of quartz, albite, enstatite, microcline, hematite, and cassiterite together with several naturally occurring sulfates and sulphides at temperature up to 600°C. and at pressures up to 30,000 psi. At 500°C. and 20,000 psi albite was decomposed as indicated by the molecular ratio of the material dissolved

in the condensate. At 30,000 psi, however, the materials appeared in the condensate in essentially the albite composition, giving an average solubility of about 0.27 wt. per cent. Enstatite was definitely decomposed by the hydrothermal treatment while microcline did not approach as closely the ideal mineral ratio in solution as did albite at 30,000 psi. The solubility of the sulfates varied from 0.002 per cent for anhydrite ( $\text{CaSO}_4$ ) at 500°C. and 15,000 psi to 0.43 per cent for  $\text{Na}_2\text{SO}_4$  at the same temperature and pressure. Cassiterite and the sulphides showed practically negligible solubility.

A commercial method for the synthesis of industrial diamonds is claimed (80) in a British patent. The process involves dissolving a specially purified carbon prepared from lignin in a commercial wrought iron free from oxides followed by a rapid chilling of the molten mixture. The iron is then slowly liquefied under vacuum and the diamonds are sifted out. The method differs somewhat from the Moissan process in that a different form of carbon is used and this is heated in an induction furnace under vacuum or in an inert atmosphere nearly to its volatilization point before the iron is poured in and mixed.

The system  $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$  has been reported by Miller (81) while hydrothermal studies on the same system with the addition of MgO were carried out by Schloemer (82). Both systems are of geological significance.

The existence of a compound  $\text{CrOOH}$  in system  $\text{Cr}_2\text{O}_3\text{-H}_2\text{O}$  has been confirmed by Laubengayer & McCune (83) who prepared the material by hydrothermal synthesis. The compound decomposes at about 430°C. Somewhat above this temperature rhombohedral  $\text{Cr}_2\text{O}_3$  is the stable phase. There is evidence of the existence of a cubic chromium oxide isomorphous with  $\gamma\text{-Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ .

Phase transitions of barium titanate and related ferroelectric substances have aroused considerable interest because of the widespread use of such materials in electronic instruments. The dielectric properties of these materials change when a polymorphic transition occurs. The method of measuring the change in the dielectric constant of such a material with temperature can be employed as both a means and an end to study these inversions: for example, the method employed by Roi (84) to study phase transitions of the barium titanate at 120° and by Shirane & Suzuki (85) and Shirane & Takeda (86) in investigating transitions in barium lead titanate and other ferroelectric materials. Buerger (87) has discussed disordering mechanisms occurring in crystals due to temperature motion. These he describes as the cause of thermal transformations.

The melting point of titanium dioxide of extremely high purity was redetermined by St. Pierre (88) to be  $1840^\circ \pm 10^\circ\text{C}$ . Lower melting temperatures previously reported by other investigators were attributed by him to the effect of the reduction of  $\text{TiO}_2$ .

Titanium carbide is a refractory material sometimes employed in "cermet" (ceramic-metal) bodies whereas boron carbide is characterized by its

extreme hardness. At temperatures above 1920°C. these two carbides react to form  $\text{TiB}_2$ , carbon and a higher boride of unknown composition [Greenhouse, Accountius & Sisler (89)].

Goldschmidt (90) introduced the term "model structures" many years ago to indicate a particular type of isomorphism in which both the anions and cations are different in the two structures compared. For example,  $\text{BeF}_2$  is the model structure for  $\text{SiO}_2$ , and  $\text{MgF}_2$ , the model for  $\text{TiO}_2$ . Osborn (91) has extended the terminology to certain fluoride and oxide systems in which the components are models and which show a marked similarity in phase equilibrium relations. Examples of two pairs of these "model systems" are the systems  $\text{MgF}_2\text{-BeF}_2$  and  $\text{TiO}_2\text{-SiO}_2$ , and  $\text{CaF}_2\text{-BeF}_2$  and  $\text{ZrO}_2\text{-SiO}_2$ . Not all systems with components that are models show this resemblance in phase diagrams, however, as indicated by the fact that the diagrams for the systems  $\text{KF-MgF}_2$  and  $\text{BaO-TiO}_2$  are quite different.

The existence of a monoxide of silicon has been known for some time [Potter (92)], and recent studies point toward the existence also of lower valence oxides of aluminum. Brewer & Searcy (93) observed that a gas having the composition  $\text{Al}_2\text{O}$  was evolved when  $\text{Al}_2\text{O}_3$  was heated with aluminum or with another reducing metal whereas heating  $\text{Al}_2\text{O}_3$  alone resulted in the evolution of  $\text{AlO}$ . Beletskil & Rapoport (94) also independently observed the formation of an oxide having the approximate composition  $\text{Al}_2\text{O}$ . On reduction of  $\text{Al}_2\text{O}_3$  by carbon in the presence of  $\text{SiO}_2$  at high temperatures (above 1800°C.) and low pressures (1 mm. of mercury) the oxide condenses in the form of crystals above the charge.

A new compound,  $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$ , reported by Morey (95), was discovered in studying the system  $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$  which is of primary interest to glass technologists. Extensive studies of the borate glass systems have likewise been made by Menzel & Adam (96). Germania is also a glass-forming oxide, and glasses in the system  $\text{Na}_2\text{O-CaO-GeO}_2$  showed high transparency to the infrared and opacity toward the ultraviolet (Parikh & Simpson (97)). There is evidence that the Ge-O bond is weaker than the Si-O bond. A soda-silica compound having a silica-soda ratio between 9.4 and 13.1 to 1 was discovered by McCulloch (98) while further work on the system barium oxide-alumina was reported by Toropov & Galakhov (99).

Four oxides of uranium were noted by Hering & Perio (100) on heating  $\text{UO}_2$  in capsules at selected temperatures between 120° and 900°C. The phases identified were (a) a cubic phase  $\text{UO}_2$ , with a variable composition extending to  $\text{UO}_{2.33}$  at 120°C.; (b) a cubic phase  $\text{U}_4\text{O}_9$ ; (c) a tetragonal phase varying in composition with temperature from  $\text{UO}_{2.4}$  to  $\text{UO}_{2.3}$  and stable up to 500°; (d) an orthorhombic phase  $\text{U}_4\text{O}_9$  whose composition range also increased with temperature. A continuous series of solid solutions exists between  $\text{UO}_2$  and  $\text{CeO}_2$  [Magneli & Kihlborg (101)], while in the same system over the range 0-63 mole per cent  $\text{UO}_2$  a fluorite phase is formed with lattice constants ranging from 5.399 to 5.431 Å [Hund, Wagner & Peetz (102)].

Hund & Peetz (103) also reported a similar fluorite structure in the system  $U_3O_8$ - $Er_2O_3$  in range from 27.0 to 66.7 mole per cent  $Er_2O_3$ , with lattice constants from  $5.349 \pm 0.001$  Å for 26.6 mole per cent  $Er_2O_3$  crystals to  $5.303 \pm 0.001$  Å for the crystals containing the highest percentage of  $Er_2O_3$ . Similar solid solutions of the fluorite type were reported by Hund (104) for the composition range 10–63 mole per cent  $Y_2O_3$  in the system  $ZrO_2$ - $Y_2O_3$ .

The constitution of portland cement has been the object of extensive investigations in the United States and Europe over a considerable number of years [Bogue (105)]. Commercial portland cement consists essentially of very finely ground clinker together with about 3 to 5 per cent of gypsum. The average cement clinker contains from 10 to 12 components so that even the anhydrous system is an extremely complex one. The general approach to its solution has been to study first the simpler ternary systems and then to progress from these to the quaternary and so on to the more complex clinker systems. These multicomponent systems present difficulties not only in their investigation but also in the representation of the data obtained. Bogue (106) has discussed the methods employed in exploring and in representing multicomponent systems. For systems up through four components, graphical methods of representation may be used, while for the more complex systems it is necessary to resort to a mathematical treatment of the data such as that developed by Dahl (107, 108) in order to represent the system fully.

In spite of the large number of components present in commercial portland cement clinkers, the latter consists principally of three crystal line phases: tricalcium silicate, dicalcium silicate, and tricalcium aluminate. These compounds are seldom present in commercial clinker as the pure phases, but ordinarily contain other components in solid solution. Jeffery (109) has deduced that pure tricalcium silicate has a trigonal pseudostructure, and that "alite" (tricalcium silicate containing a small amount of  $Al_2O_3$  and  $MgO$  in solid solution) is monoclinic below  $825^\circ C$ . At  $825^\circ C$ , the latter inverts to a trigonal form while pure tricalcium silicate shows two transitions, one at  $923^\circ C$ , in which it goes from a triclinic to either a monoclinic or trigonal form, and another at  $980^\circ C$ , where it inverts to a trigonal form, with or without positive rotation of anions. Nurse (110) has discussed the four polymorphic forms of dicalcium silicate,  $\gamma$ ,  $\beta$ ,  $\alpha'$  and  $\alpha$  recently investigated by Trömel (111), believed to exist in the temperature range  $0$ – $1600^\circ C$ . Midgley (112) has determined that  $\beta$  dicalcium silicate is monoclinic. The number of polymorphic forms of dicalcium silicate and the temperatures at which inversions occur have been the subject of some disagreement among investigators in the past. It is evident, however, that these inversion temperatures are altered considerably by solid solution which may occur, particularly in the high-temperature forms [Newman & Wells (113); Greene & Bogue (114)].

Tricalcium aluminate is presumably cubic. A detailed structural deter-

mination from x-ray studies of single crystals of this compound is being carried out by Ordway (115). The remaining constituents of portland cement clinker such as  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ , etc., although comprising only about 10 per cent of the clinker, may, nevertheless, have a very important effect on its constitution. Interstitial phases in portland cement clinker have been discussed by Insley (116) while summaries of current knowledge on the iron (ferrite) and the alkali phases are discussed by Malquori & Cirilli (117) and Newkirk (118), respectively.

Studies of the reactions which occur during the hydration of portland cement present an even more complex problem. A considerable amount of useful information should be gained, however, by considering the simple ternary system  $\text{CaO-SiO}_2\text{-H}_2\text{O}$  as a model representing the first approximation to the phenomena of hydration of portland cement (Brunauer (119)). Portions of the system have been studied by many investigators. A comprehensive review of the reactions and thermochemistry of cement hydration is given by Steinour (120). Heller & Taylor (121) and Taylor (122) have recently reported extensive studies on hydrated calcium silicates, and Bernal (123) has studied structures of ten of these phases. Hydrothermal reactions in the system  $\text{CaO-SiO}_2\text{-H}_2\text{O}$  are of chemical and geological interest as well as having industrial significance for the manufacture of sand-lime bricks.

A new compound, tristrontium silicate, was reported by Nurse (124). Substitution of strontium for calcium in cements may be of value in increasing their resistance to attack by sea water or sulfates.

#### METALLIC SYSTEMS

Most of the early work in high temperature phase equilibria was in the application of the principles of Gibbs (125) by the methods proposed by Roozeboom (126) to the investigation of metallic systems, and this has continued to be a major field of endeavor. The classical methods of studying metallic systems are by the use of cooling curves and by the microscopic examination of quenched charges. Quenched specimens are given a surface polish by mechanical or electrolytic methods and this is followed by an etching treatment to bring out the desired phase detail. Observation is then made under the microscope by reflected light. More recently, reflected *polarized* light has been used to bring out structural details, particularly in certain anisotropic materials for which satisfactory etching techniques have not been developed, e.g., uranium metal [Mott & Haines (127)]. X-ray diffraction and microradiographic techniques are also widely employed in present-day studies of metals. For example, Taylor & Floyd (128) used these two techniques in their work on the binary systems nickel-chromium and nickel-titanium, Magnetic analysis may also be used in the investigation of certain systems, for example, in the system palladium-zinc (Nowotny, Bauer & Stempfll (129)), and the system nickel-manganese-antimony [Castelliz (130)]. Neutron diffraction studies have been made of certain



intermetallic compounds, in particular,  $UBe_{13}$  and  $ThBe_{13}$  [Koehler, Singer & Coffinberry (131)].

Measurements of changes in electrical resistivity or specific heat also provide information on metallic phase changes [Taylor & Hinton (132)]. Darling, Mintern & Chaston (133) made measurements of the change in electrical resistance of wire samples with temperature to supplement data obtained by other methods in re-studying the system gold-platinum. Their work confirmed that of some of the early investigators in that a continuous series of solid solutions was found to exist between the two metals in the region just below the solidus. Below  $1258^{\circ}\text{C}$ ., however, there is a miscibility gap.

Data obtained by means of cooling curves are always subject to a certain amount of error due to supercooling. While this phenomenon is not as serious in metallic systems, it may occur. In any case, it is necessary that cooling be sufficiently slow to allow equilibrium to be reached at each stage if a true equilibrium diagram is to be obtained. In metallurgical phase diagrams it is also common to show metastable relationships, sometimes with the construction with an additional metastable phase diagram. For example, Hilliard & Owen (134) interpreted the results of their own and previous investigations of the system iron-carbon-silicon in terms of a double ternary diagram showing both stable and metastable phases. Graphite and the iron-carbide phase ( $Fe_3C$ ) were indicated as the stable and metastable carbon phases, respectively. Despite the volume of literature on this system, there has been considerable disagreement about the location of certain invariant points and the low temperature phase relationships in the system. The studies of Hilliard and Owen were limited to constant-silicon sections of the metastable iron-carbon-silicon diagram taken at 2.3, 3.5, 5.2, and 7.9 per cent silicon. The invariant point at which ferrite, austenite and the carbide phase are in metastable equilibrium with liquid was relocated at 8.35 per cent silicon and 1.92 per cent carbon. The temperature for this point was re-established as  $1145^{\circ}\text{C}$ . and the compositions of the three solid phases were redetermined. The new diagram is consistent with experimental evidence that the carbide phase consists essentially of pure  $Fe_3C$ .

In the system iron-nickel-aluminum, permanent magnets can be made from alloys approaching the composition  $Fe_2NiAl$ . A satisfactory explanation for this phenomenon could not be given on the basis of early work. Bradley & Taylor (135, 136) and Kiuti (137) observed that on cooling, the ordered body-centered cubic solid solution dissociated to form two phases, one ordered ( $\beta'$ ) and the other disordered ( $\beta$ ). In recent studies by Bradley (138) of the transformation of the  $\beta$  and  $\beta'$  phases, it was determined that for the state of highest coercivity, the matrix consists of a nonmagnetic ordered  $NiAl$  ( $\beta'$ ) phase containing a finely-dispersed precipitate of the lamellar ferromagnetic  $\beta$  phase which can consist of almost pure iron. Bennett (139) attributes changes in coercive force in certain iron-aluminum alloys in the



region 450° to 560°C. to the presence of mixed regions of order and disorder which give rise to internal stresses at about 500°C. According to Bennett, these stresses contribute to the relatively large increase in coercive force in this region.

In the high-aluminum portion of the system aluminum-chromium-iron, only  $\text{CrAl}_7$  with iron in solid solution and  $\text{FeAl}_3$  with chromium in solid solution enter into equilibrium with the aluminum-rich solid solution, there being no ternary compound in this region [Pratt & Raynor (140)]. A strong analogy exists between the aluminum-rich alloys in this system and those in the system aluminum-chromium-manganese. In the low-chromium region (up to about 9.5 per cent chromium by weight) of the system aluminum-chromium-zinc, no ternary compounds occur, and the primary-phase region for  $\text{CrAl}_4$  is extensive [Harding & Raynor (141)]. This compound crystallizes from the melt at zinc contents exceeding 99 per cent.

Taylor & Floyd (142) studied the equilibrium relationships in the nickel-rich alloys (containing more than 50 atomic per cent of nickel) in the nickel-titanium-aluminum system over the range 750°–1150°C. A ternary  $\text{Ni}_2\text{TiAl}$  phase,  $\beta_3$  with a  $\text{Cu}_2\text{ZnAl}$ -type of structure was observed in equilibrium with the  $\beta_1$   $\text{NiAl}$  and  $\beta_2$   $\text{NiTi}$  phases which have CsCl-type structures. At 750°C. the face-centered cubic primary nickel solid solution,  $\gamma$ , contains more than 12 atomic per cent of titanium and aluminum in solution.

The presence of small amounts of cadmium, indium, or tin in aluminum is associated with the age hardening of aluminum alloys. Hardy (143) has shown that cadmium and indium have maximum solubilities in aluminum of 0.45 and 0.11 weight per cent, respectively, at their monotectic temperatures while the solubility of tin in aluminum increases to a maximum of about 0.1 per cent at 610°C. and then decreases with further rise in temperature.

The equilibrium diagram for the ternary system aluminum-indium-tin was only recently determined by Campbell *et al.* (144). The addition of aluminum to the binary system has but little effect on the nature of the solid phases. Campbell *et al.* concluded that in the ternary system aluminum does not enter into indium-tin solid solutions to an extent greater than 5 per cent and probably not at all. A portion of the equilibrium diagram for the system copper-indium in the region 25 to 35 atomic per cent indium was re-examined by Reynolds, Wiseman & Hume-Rothery (145). Stubbs *et al.* (146) confirmed the existence of the compounds  $\text{In}_2\text{S}_3$ ,  $\text{InS}$  and probably  $\text{In}_3\text{S}_4$  and  $\text{In}_5\text{S}_8$  in the system  $\text{In-In}_2\text{S}_3$ . Of these all but  $\text{In}_3\text{S}_4$  are stable at room temperature.  $\text{In}_2\text{S}_3$  is shown in the phase diagram as melting congruently but is said to melt "with decomposition." The indium-arsenic system has been studied by Liu & Peretti (147).

The solubility of silicon in  $\alpha$  and  $\beta$  zirconium was shown by Lundin, McPherson & Hansen (148) to be low as is also the case of the solubility of chromium in  $\alpha$  and  $\beta$  zirconium [Hayes, Roberson & Davies (149)]. In the

latter system the solubility of chromium in  $\alpha$  zirconium is negligible while that in  $\beta$  zirconium at the eutectic temperature (1380°C.) is about 6.2 per cent. On the other hand, the solubility of tin in  $\beta$  zirconium is relatively high being 21 per cent at the Zr-Cr<sub>3</sub>Sn<sub>3</sub> eutectic [McPherson & Hansen (150)], while that in  $\alpha$  zirconium ranges from 9 per cent at 980°C. to 1.5 per cent at 599°C.

In the system chromium-tungsten a continuous series of solid solutions is formed above 1500° [Greenaway (151)]. Below this temperature two limited solid solutions exist. Lead and uranium were observed by Teitel (152) to form two intermetallic compounds, UPb<sub>3</sub> and UPb.

The system palladium-cadmium was investigated by Nowotny, Stempf & Bittner (153), while that of copper-gallium was studied in the range 30 to 100 atomic per cent of gallium by Betterton & Hume-Rothery (154). This completes the phase diagram for the latter system since the region 0 to 30 atomic per cent gallium was previously investigated by Hume-Rothery, Mabbot & Channel-Evans (155) and by Hume-Rothery & Raynor (156). Phase relations for copper-gallium resemble those of copper-aluminum.

The system nickel-vanadium was explored in the region 0 to 60 atomic per cent vanadium by Pearson & Hume-Rothery (157). There exists a wide range of solid solubility of vanadium in nickel (up to about 42 atomic per cent vanadium at 1200°C.). A eutectic occurs at 51 atomic per cent vanadium and 1202°C., at which temperature the liquid is in equilibrium with the  $\alpha$  (nickel-base) solid solution and a second solid solution having the same general type of crystal structure as the phase in iron-chromium alloys.

A metal which has received considerable attention in the past few years is titanium. Formerly used mainly in elements of radio tubes and to increase strength in steel alloys, the metal is now finding a variety of applications in which its relatively low specific gravity (4.5) and its high-temperature strength give it a decided advantage.

Finlay (158) has proposed seven phase designations for titanium-rich alloys based on equilibrium diagrams. These classifications illustrated by corresponding binary systems are as follows:  $\alpha$ - $\beta$  isomorphous, titanium-zirconium;  $\beta$ -isomorphous, titanium-molybdenum, tungsten, tantalum or niobium; terminal  $\beta$ -isomorphous, titanium-manganese, iron, and chromium; peritectic, none known; eutectoid, titanium nickel; terminal peritectoid, titanium-carbon, oxygen, or nitrogen, and intermediate peritectoid, none known. Pure titanium undergoes an  $\alpha$ - $\beta$  transformation at 800°C. (159). Titanium and vanadium form a complete series of solid solutions above 885°C. [Pietrokowsky & Duwez (160)]. The presence of vanadium depresses the  $\alpha$ - $\beta$  transformation as do chromium, manganese, nickel, and cobalt [McQuillan (161); Van Thyne, Kessler & Hansen (162)]. The titanium end of the titanium-aluminum phase diagram has now been completed [Bumps, Kessler & Hansen (163)].

Hagg & Kiessling (164) studied the distribution of metals between phases

in equilibrium with each other in ternary systems  $\text{Me}_1\text{-Me}_2\text{-B}$ , where  $\text{Me}_1$  and  $\text{Me}_2$  are members of the first series of transition metals. They found that the metal with the lower atomic number is always concentrated in the phase richest in boron. This was taken to indicate that the strength of the  $\text{Me-B}$  bond increases with decreasing atomic number of the transition metal.

In the system  $\text{W-Co-C}$ , Rautala & Norton (165) found two double carbides  $\theta$  and  $\text{K}_1$  with compositions  $\text{Co}_3\text{W}_6\text{C}_2$  and  $\text{Co}_3\text{W}_{10}\text{C}_4$  respectively. Tentative diagrams of stable and metastable equilibria were prepared.

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## SOLUTIONS OF ELECTROLYTES<sup>1</sup>

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This review necessarily begins with the explanation that the assigned title is a misnomer in the quantitative sense. Most of the systems treated involve water as the solvent, and the physical chemistry of solutions of electrolytes is still, as far as scope is concerned, almost exactly what it was in Ostwald's day. The more we learn about water, the clearer it becomes that this liquid holds an exceptional position among solvent media, but research workers the world over persist in studying aqueous systems, and then attempt to base broad generalizations on this limited range of experience. The literature covered here (based primarily on papers included in *Chemical Abstracts*, Volume 46) essentially reports routine progress on various aspects of the problems of aqueous solutions of electrolytes, although a few new ideas did manage to squeak past the guardians so aptly christened by Kraus (108) in "Fragments of Chemistry."

### GENERAL THEORY

In 1926 Kramers (107) presented a derivation of the thermodynamic properties of electrolytic solutions which was based on the methods of classical statistical mechanics. Briefly described, he used the Milner-Coulomb sum to represent the mutual potential energy of the ions and considered an ensemble in which all possible arrangements of charges on the ions in the total volume were counted. As was well known, the classical sum diverges for point charges although short range repulsion insures convergence for real ions of nonzero size; Kramers allowed for the short range repulsion by a special modification of the potential which gave mathematical convergence of the integrals and then conveniently disappeared from the final result. In order to simplify the calculation, Kramers made certain other approximations which were clearly stated in his original paper. His final result was most gratifying; he obtained limiting square root laws for low concentrations, by methods whose generality and soundness had been long established. This result served to reassure many of the early workers, some of whom had reservations about the Poisson-Boltzmann approximation which Debye & Hückel had proposed; furthermore, no controversial charging process was involved. Unfortunately, Kramers' original paper was not conveniently accessible and was at best known by hearsay; the mathematics was also considerably more sophisticated than that of linear differential equations; and finally, the Kramers function deviated from the limiting square root tangent in precisely the opposite direction from the experimental data. Despite the fundamental soundness of the approach and despite the fact that the

<sup>1</sup> This survey of the literature pertaining to this review was concluded in December, 1952.

theory was inherently a theory for nonvanishing (rather than zero) concentrations, it has been almost completely disregarded until quite recently. Berlin & Montroll (20) have now re-examined Kramers' work and considered the consequences of eliminating Kramers' most drastic approximation. The potential energy of an ionic system is a quadratic form in the charges; Kramers diagonalized this by introducing variables  $y_j$  which are linear combinations of the charges  $\epsilon_j$ , and then assumed a Gaussian distribution of the  $y_j$ 's. As Berlin & Montroll show, this assumption leads to a far too great ensemble, in that it permits the ionic strength to range from zero to infinity. They accordingly selected as their complete ensemble that set of systems which satisfied the restriction of a fixed ionic strength. The analytical result, as might be expected, is a square root law in the limit of low concentrations. However, two significant differences from Kramers' result appear: first, the calculated curve breaks away from the limiting tangent in the same direction as the experimental data; and second, there is no "terminal" concentration above which the solution becomes physically meaningless.

The break-away is not as large or as early as that exhibited by simple salts like sodium chloride, and the theoretical result is a universal function for each valence type regardless of the specific ions. It must be remembered that the device Kramers used to avoid short range divergence was essentially a mathematical one rather than a physical one; in other words, he used a guarding function which avoided automatically any singularities for zero distance rather than the more realistic model of billiard ball ions of finite (and parametrically variable) size. The use of the latter would admittedly complicate the calculation, but it seems reasonable to expect that specific differences between different ionic species (something like the familiar  $\kappa a$  terms) would thereby appear. The terminal concentration of the original theory was also an awkward feature: in effect, its existence implied that association of ions would set in suddenly at a critical concentration  $(N/V)_{crit} = (1/27\pi) (DkT/\epsilon^2)^3$  or at 0.029 molar for 1-1 salts in water at 25°C. In the Berlin and Montroll theory, the thermodynamic functions are continuous functions of concentration at all concentrations (although discontinuities appear in their higher derivatives). Up to a concentration  $(N/V) = (1/\pi) (DkT/\epsilon^2)^3$ , the thermodynamic potential is linear in the square root of concentration; at this concentration, it goes over smoothly into a function containing an opposing logarithmic term, which causes the theoretical function to deviate from the square root limit in the direction taken by experimental data. The Berlin-Montroll critical concentration is 0.78 *M* for 1-1 salts in water at 25°C.; this is roughly five times the concentration at which Fuoss (55) calculates that association even more complicated than pairwise should be considered. If pairwise configurations of ions of finite size are examined statistically (53), a distribution function is obtained which unambiguously defines short-range ion pairs up to a critical concentration  $(N/V) = [e^{-x}x^2(2-x)/2\pi] (DkT/\epsilon^2)^3$  where  $x = 3 - \sqrt{3}$ ; for 1-1 salts in water at 25°C., this is 0.15 *M*. From the point of view of long range interaction

theory, association is, of course, a fluctuation phenomenon. As Berlin & Montroll point out, "the present theory makes it clear that one cannot avoid the introduction of the finite ion size if even the qualitative behavior of the small concentration deviations from the Debye-Hückel law is to be reproduced." It is to be hoped that this necessary refinement of the model will eventually be made, because the Kramers approach appears to be a promising potential attack on the problem of nonvanishing concentrations.

The Poisson-Boltzmann equation still continues to be a fruitful source of information about the behavior of electrolytes, despite some inherent limitations (103, 130). As originally set up by Debye & Hückel, the equation is nonlinear; as is well known, these authors derived their limiting laws by using the fact that the differential equation reduces to linear form when the electrostatic energy  $e\psi$  of an ion averages to substantially less than  $kT$ . The problem of higher concentrations (or alternatively, of higher valence types) is necessarily, therefore, bound up with a treatment of the equation in its nonlinear form. Gronwall, LaMer & Sandved (68) gave a formal solution of the nonlinear equation in terms of a series development which substantially increased the range of usefulness of the original theory (albeit at the necessary expense of considerable computational labor). Electrolytes in which one species carries a very high charge (proteins, colloidal electrolytes, and polyelectrolytes, for example) represent another case in which the simple theory cannot be applied: a potential of only 25 mv. makes the ratio  $e\psi/kT$  equal to unity, and in the domain of colloids and related substances potentials of several hundred millivolts may appear. Verwey & Overbeek (189) have summarized one treatment of this problem. Booth (26) has approached the problem of high charge densities by applying the Gronwall method to the complete Poisson-Boltzmann equation, introducing boundary conditions appropriate to several geometries which serve as bases for useful models. His results are expressed in terms of power series, in which the first (although not necessarily the largest) term is the Debye-Hückel approximation. Cases treated include planar, cylindrical, and spherical boundaries. In principle, the method will yield as many terms of the series as desired, because the technique is one of iteration. The author points out the fact that the calculation becomes impractical beyond a certain stage. Also, convergence proofs are difficult to establish. Nevertheless, Booth's results promise to be useful in a field where empiricism has by and large led theory. Booth (27) has, for example, considered the problem of the electrophoresis of spherical liquid particles, which involves much more intricate boundary conditions than the case of moving solid particles. He obtained an explicit solution for several distributions of charge on or in the sphere, subject to the approximation that  $e\psi/kT \ll 1$ , and at least indicates how a better approximation might be obtained by use of his potential theory.

DeButts (42) has presented a general treatment of the dissociation of multivalent weak electrolytes. For lower members of the series of polycarboxylic acids, for example 1,2,3-propanetricarboxylic acid, calculation of

the concentrations of the individual ionic species from the several dissociation constants by classical methods is a possible although tedious computation. When, however, the basicity becomes higher than a small integer, classical methods fail due to the inevitable high order of the algebraic equations which correlate the concentrations of the various species. By simple statistical methods, deButts shows that

$$\partial \ln n_{s-i} / \partial (-\ln a_{H^+}) = i - \alpha s \quad \text{I}$$

where  $n_{s-i}$  is the number of ions of charge  $i$ ,  $s$  is the basicity of the acid,  $a_{H^+}$  is hydrogen ion activity, and  $\alpha$  is the average degree of ionization. Equation I states that the concentration of a given species reaches a maximum when the average degree of dissociation equals the ratio of its charge to  $s$ , the maximum possible charge. The relative concentration of any species of ion may be obtained either from an analytic relationship between  $\alpha$  and hydrogen ion activity, or more practically, by numerical integration of potentiometric titration curves. In general, one has

$$\text{pH} + \log (1 - \alpha) / \alpha = \text{p}K_0 + 0.4343 \Delta F_a / kT \quad \text{II}$$

where  $K_0$  is the inherent ionization constant and  $\Delta F_a$  is the electrical free energy of ionization; the latter is of the form  $\alpha f(R, w)$ , where  $R$  measures the size of the ion at degree of dissociation  $\alpha$  and  $w$  is ionic strength. By combining Equations I and II and expanding the exponential, a theoretical distribution curve is obtained, which is not sensitive to  $s$  when  $s$  is large (*i.e.*, in the range of polymeric acids), but which is sensitive to the free energy term. DeButts applied his method to the data of Arnold & Overbeek (5) on the titration of polymethacrylic acid in the presence of potassium chloride, and was able to show (a) that electrostatic interaction in the coil had to be considered (*i.e.*,  $f \neq 0$ ); (b) that the presence of  $10^{-4}M$  potassium chloride produced too much electrostatic screening to permit application of the Katchalsky & Gillis formula (100); and (c) that the Cohn & Edsall approximation (36) of the macromolecule by a charged sphere with a Debye-Hückel atmosphere was in fair agreement with the observed titration curve.

#### THERMODYNAMIC QUANTITIES

Bender & Biermann (18) have made a series of measurements of the heat of neutralization of sodium hydroxide and hydrochloric acid in the range 3.0 to 16.4 molal. The paper contains a critical discussion of relevant data in the literature. The authors estimate an accuracy of at least 0.1 per cent in the figure  $-13,320$  calories per mole which they propose as the heat of neutralization at  $25^\circ\text{C}$ ., and extrapolated to infinite dilution. The result agrees to nearer than 10 cal. per mole with the value calculated from the classical measurements of Richards & Rowe (143) at 1.110 and 2.220 molal. At 13.85 molal, solid sodium chloride is precipitated during the reaction; the theoretically expected discontinuity in the slope of the  $\Delta H$  vs.  $m$  curve is, however, invisible due to the low heat of crystallization of sodium chloride.

The system sulfuric acid-water has been studied in some detail by Giauque and his co-workers (112, 114, 146). The heat capacity and entropy of anhydrous sulfuric acid and of its three hydrates were measured over the range 15–300°K. The trihydrate was obtainable as a glass, so that a comparison of the glassy and crystalline forms was possible; at 0° K, the former retains an amount of disorder corresponding to 5.9 entropy units per mole. Work on the crystalline trihydrate was complicated by its unstable melting point: at about 0.1° below this temperature, the trihydrate is in equilibrium with tetrahydrate and solution (61). For the compounds  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , the melting points are respectively 283.53, 281.64, and  $233.69 \pm 0.05^\circ\text{K}$ ; the corresponding heats of fusion are 2560, 4646, and 4360 cal. per mole, and the molar entropies are 37.49, 50.49, and 66.14 cal. per degree. The transition temperature of the trihydrate is  $236.72^\circ\text{K}$ ., where the heat of fusion is 5782 cal. per mole. Solutions of sulfuric acid in water from one molal to pure acid were measured at  $25^\circ\text{C}$ . in a differential dilution calorimeter of new design; some systems were also measured at  $-20^\circ\text{C}$ . The heat capacity of the solutions and the partial specific heat content of water were calculated from the data; the former shows a small but sharp cusp at 100 per cent acid as a result of molecular dissociation, and the latter drops by about 8000 cal. per mole on going from  $\text{H}_2\text{O}$ -excess to  $\text{SO}_3$ -excess. One surprising result of this series of investigations was the observation (113) that, contrary to the conclusion based on earlier less precise measurements, the conductance minimum of the system occurs at  $99.996 \pm 0.001$  weight per cent acid, rather than exactly at pure  $\text{H}_2\text{SO}_4$ . Likewise, the next minimum in conductance does not appear exactly at the monohydrate (84.48 per cent  $\text{H}_2\text{SO}_4$ ) but at  $84.63 \pm 0.05$  weight per cent.

A thermochemical approach to the problems of ionic solvation and of relative base strengths of solvents was made at the Argonne National Laboratory (101), where the heats of solution of the di-, tri-, and hexahydrates of uranyl nitrate in water and in a variety of alcohols, ethers, ketones, and esters were measured. When a given hydrate is added to an organic solvent, some or all of the water may be displaced; the thermal effect observed is a measure of this competition. In ethers, for example, two molecules of water are always retained by the uranyl ion, while in alcohols the water is completely replaced. Ketones and esters are in general poorer competitors for water than ethers and alcohols: this may be demonstrated by comparing the heat effect on adding a given amount of water to a pure solvent and to the same solvent containing uranyl dihydrate. The differential effect is, for example, only 0.1 kcal. per mole for diethyl ether and isobutanol, and runs to three or more kcal. per mole for several ethyl esters. The sequence of electron donating ability based on this thermochemical work agrees with the work of Gordy & Stanford (65) on the displacement of the infrared bands of deuterio-methanol by other organic liquids.

Salts of higher valence type are of especial interest because they may be expected to show large deviations from simple theory. Spedding &

Miller (167) have recently reported the first data on the heat capacities of 3-1 electrolytes, using aqueous solutions of cerium and neodymium chlorides as examples. Excellent agreement between theoretical and experimental limiting slopes for the relative apparent molal heat capacity and heats of solution were found; as concentration increased, both salts showed positive deviation from the limiting law for heats of solution, with somewhat greater deviations for neodymium. The rare earths promise to be useful in correlating association and hydration with ionic charge and size, because they represent a series of elements of fixed charge and variable radius. A number of additions have also been made to the knowledge of simpler salts. Eigen & Wicke (47) reported the specific heats of aqueous solutions of sodium chloride, lithium bromide, and magnesium chloride over a wide range of concentration and temperature (up to 140°C.). An interesting feature of their results is the appearance of a maximum at 70°C. in the apparent molar heat. Samoilov (94, 97, 147) and his co-workers have measured the heats of solution in water of potassium chloride and magnesium sulfate at several temperatures between 25 and 45°C. After these conventional calibrations, mixtures of electrolytes were investigated. For example, the heats of solution of a variety of 1-1 and 1-2 salts in solutions of hydrochloric acid of varying concentration  $m$  were measured. Those salts with positive heats of solution  $L$  showed a linear decrease of  $L$  with increasing  $m$ , while those with negative  $L$  showed a linear increase. As the authors point out, relative hydration of the various ionic species must be one of the controlling variables.

Quantitative thermochemical data on nonaqueous systems continue to be rare. Mulder & Schmidt (128) report heats of solution in liquid ammonia at -33.4°C. of a series of guanidine salts, and of potassium iodide, potassium amide, potassium thiocyanate, and ammonium thiocyanate. The guanidine salts all show heats of solution in the same range as ammonium salts and other strong electrolytes. The heat of solution of potassium amide, on the other hand, is markedly lower. It is known that potassium amide is a weak electrolyte in ammonia. Heats of neutralization of potassium amide by various ammono-acids were also determined; the average of four acids gives  $\Delta H = 26.5$  kcal. per mole. This is larger by 6.1 kcal. than the single earlier datum (109) in the literature, and should replace it. Since the measured heat of neutralization contains the (opposing) energy of dissociation of potassium amide, it is seen that heats of neutralization in ammonia run far higher than in water. Several heats of formation were also measured:  $\text{Na}_2\text{Se}$ , 85 kcal. per mole and  $\text{Na}_2\text{S}_2$ , 100 kcal. per mole.

Suzuki (178, 179) has determined the solubility products and free energies of silver azide, thallous azide, and thallous thiocyanate by measurement of the electromotive force of cells with liquid junction. The solubility products found are  $\text{AgN}_3$ ,  $2.88 \times 10^{-9}$ ;  $\text{TlN}_3$ ,  $2.19 \times 10^{-4}$  and  $\text{TlCNS}$ ,  $1.70 \times 10^{-4}$ , all at 25°C. The activity coefficients of thallous bromate were determined (177) by measuring solubilities in the presence of other electrolytes with and



without a common ion; its solubility product at 25°C. is  $1.18 \times 10^{-4}$ .

The activity coefficient ratios of nitric acid and silver nitrate (25) over the range 0.1 to 1.0 molal in total ionic strength were determined by measurements of cells of the type:  $\text{Ag}|\text{AgCl}|\text{HCl}(0.2M)|\text{glass}|\text{HNO}_3(m_1), \text{AgNO}_3(m_2)|\text{Ag}$ , in which the glass electrode served to indicate the activity of the hydrogen ion. This ratio  $\gamma(\text{HNO}_3)/\gamma(\text{AgNO}_3)$  increases with increasing ionic strength. The data were used in the analysis of equilibria (24) in cation exchange resins. Concentration cells with transference were used by Speding, Porter & Wright (166) to measure the activity coefficients of the chlorides of lanthanum, cerium, praeosodymium, neodymium, samarium, europium, erbium, and ytterbium. Up to about 0.1 *N*, the data conform to the Debye-Hückel equation for ions with finite size. For the above eight rare earths, the *a*-values range from 5.60 for europium to 5.92 for neodymium; the differences are hardly significant. The average ion size corresponds approximately to the sum of the crystallographic radius plus the diameter of one water molecule. Radioactive tracers were used by Betts & MacKenzie (21) to measure the activity coefficients of the alkali chlorides in the presence of hydrochloric acid, by equilibration with ion exchange resins. Like Samoilov (147), they conclude that competitive hydration of cations is involved. The results were discussed from the point of view of the hydration theory suggested by Stokes & Robinson (172). Finally, in connection with activity coefficients, attention is called to a review by Long & McDevit (118) entitled "Activity Coefficients of Nonelectrolyte Solutes in Aqueous Salt Solutions." The paper contains a bibliography of 180 references and an appendix which summarizes in tabular form experimental studies of salt effects on polar and on nonpolar nonelectrolytes.

Precision values (reproducible to parts per million) have been reported by MacInnes & Dayhoff (122) for the densities of solutions of potassium chloride and of sodium and potassium iodides, as well as for solutions of iodine in the alkali iodide solutions. They used a magnetic float, the motion of which could be controlled to high precision by control of the current through a solenoid surrounding the apparatus.

Solubility determinations have been used in a variety of ways to explore molecular interaction. The solubility of benzene in aqueous salt solutions has received considerable attention (125, 151, 155); despite the fact that benzene is a relatively inert substance, different electrolytes affect its solubility in markedly different ways. For example, sodium sulfate or barium chloride are strong salting-out agents, while tetramethyl ammonium bromide considerably increases the solubility. McDevit & Long (125) make the suggestion that the differences arise from differences in behavior of the salt solution itself towards the cavity occupied by the molecule of organic solute, and that dipolar or other fields of the latter play only a secondary role. On the assumption that the organic solute merely occupies volume, the free energy of transfer of a solute from water to salt solution has been calculated,

using a procedure similar to that of Hildebrand & Scott (81). The underlying idea is that a compression (contraction) usually occurs when electrolyte is added to water; it therefore is more difficult to inject an organic solute into a salt solution than into water. Predicted relative results agree with experiment, both for anion and cation series, and also for salting out or in; if reasonable allowance is made for the fact that the solution is not a continuum, absolute agreement can be obtained. McDevit & Long's theory is a marked improvement over the Debye & McAulay's theory in that it specifically allows for properties of individual ions; on the other hand, the effect of organic solute on ionic free energy via the dielectric constant cannot be neglected in a final theory, nor, as Gross (151) and his co-workers point out, may short range forces among solute molecules, water molecules, and ions be disregarded.

Reynolds & Argersinger (142) have shown that exact determination of the solubility minimum of a slightly soluble electrolyte in a soluble salt with a common ion (e.g., AgOH in NaOH) permits calculation of (a) the number of complexing anions per central atom and (b) the dissociation constant of the complex. The solubility product must be known also, and the method is inapplicable if several associative equilibria (e.g.,  $\text{PbCl}_2^-$  and  $\text{PbCl}_4^{--}$ ) are competing for the cation. Jonte & Martin (78) investigated the formation of complexes between silver chloride and chloride ion, using radioactive silver as a means of determining very low concentrations. They found no evidence for a complex ion higher than  $\text{AgCl}_2^-$ . The minimum in silver chloride solubility is about  $5 \times 10^{-7} M$  at a chloride ion activity of  $2 \times 10^{-3}$ . An interesting byproduct of the study was the value of  $4.9 \times 10^{-4}$  for the dissociation constant of silver chloride; this low value confirms the general notion that silver chloride is a weak electrolyte. Gledhill & Malan (63) have made an extremely careful determination of the specific conductance of saturated silver chloride solution; from their result and the equivalent ionic conductances of silver ion and chloride ion, they compute a saturation concentration at 25°C. equal to  $1.334 \pm 0.005 \times 10^{-6} N$ , which corresponds to a solubility product of  $1.77 \times 10^{-10}$ . Their result agrees exactly with Owen's (132) earlier potentiometric result.

Solubility can increase in the presence of salts either because of a decrease in activity coefficient of the solute or because of complex ion formation. Interpretation of solubility data is further complicated if the solute is a weak electrolyte. Silver propionate and silver butyrate (141) are more soluble in silver nitrate solution than in water, but the data cannot, as the authors mention, be analyzed in detail until the dissociation constants of the silver carboxylates are known.

Solubilities of electrolytes in nonaqueous solvents are all too scarce in the literature. Vernon & Walck (188) measured the solubility of a series of quaternary halides in methanol and in *n*-butanol; in the range tetramethyl to tetrabutyl, the former was the better solvent, but the indication is that



butanol would be the better solvent for higher members of the series. Altaba (4) determined the solubilities of a number of alkaline earth halides in acetone; individual ionic characteristics show up quite sharply in the temperature coefficients, as well as in the absolute solubilities. For example, the solubilities at 20°C. of  $\text{MgBr}_2$ ,  $\text{CaBr}_2$ , and  $\text{SrBr}_2$  are 0.53, 2.75 and 0.62 gm. per 100 gm. acetone, while the temperature coefficients of solubility are respectively positive, zero (at 25°C.) and negative for these three salts.

Acid-base and dissociation equilibria have been studied in a variety of systems. The practical pH scale is defined in terms of the hydrogen electrode, but glass electrodes, standardized by known buffer solutions, are more convenient for general use. Recently, the Bureau of Standards has recommended (12) standard solutions for the very low and very high pH ranges, where reliable reference solutions have been urgently needed. For pH of 2.15 at 25°, 0.01 *M* potassium tetroxalate was selected; 0.01 *M* trisodium phosphate has a pH of 11.72. Others are given in the intermediate ranges. Bates and co-workers (13) have made a careful study of the pH of solutions of potassium acid tartrate from 0 to 60°C; at 25°C, the buffer range is around pH 3.5. Hart (77) reports that 0.4 unit should be added when deuterium chloride is measured electrochemically in order to obtain "true pD" values; about 0.7 to 0.8 should be added in colorimetric work. The glass electrode has been investigated further by Beck & Wynne-Jones (16) who distinguish two contributions to the total potential: (a) an instantaneous potential due to the hydrogen ion activity of the environment and (b) an asymmetry potential which arises from exchange of ions or water between the glass and the solution. The latter varies with time and due precautions must therefore be taken in using glass electrodes, especially at the extremes of the pH scale. This is confirmed by the work of van Schuylenborgh & Vervelde (156) who show that the glass electrode may be used to determine the activity of sodium or potassium ions in solutions of high pH. They assume that the glass behaves as a weak acid, and that the observed potentials are Donnan membrane potentials.

The following is a catalogue of a number of dissociation studies: (117) cupric salts of a series of 17 monocarboxylic acids; (89) benzoic acid in water at 20, 25, 30, and 35° by use of the quinhydrone electrode; (102) sulfamic acid in water at 5° intervals between 10 and 50°; (136) pyruvic and oxaloacetic acids at 25 and 37°; (123) 5,5-diethylbarbituric acid from 0 to 60° by using cells without liquid junction; (149) *d*-tartaric acid at 25°; (185) isophthalic, terephthalic, and chloranilic acids by means of spectrophotometric measurements in the near ultraviolet; (186) glucose, mannitol, and sorbitol at 0 and 18° by use of both hydrogen electrode and glass electrode; (62) hydrolysis of nickelous and cobaltous ions to  $\text{MOH}^+$ ; (148) a series of biguanides and dibiguanides; and (145) a series of polymethylene polyamines ranging from  $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$  to compounds with four nitrogen atoms. The last mentioned paper presents an interesting correlation between base

strength and ease of quaternization. The latter is an ionic nucleophilic reaction and electrostatic forces around the nitrogen also determine basicity; the same electron pair on the nitrogen is involved in both reactions. If  $\Delta pK$  represents the interval between the  $pK$ 's of two particular nitrogens, then  $\Delta pK$  decreases from 3.1 for two methylenes between basic nitrogens to about unity for seven or eight, as the charged centers become further apart and influence each other correspondingly less. When more than two nitrogens are present in a molecule, the  $\Delta pK$ 's are approximately additive. The larger the  $pK$ , the faster the quaternization. Thus, in hexamethyl-triethylenetetramine, the terminal nitrogens quaternize rapidly with methyl iodide at 25°C. in ethanol, one of the medial nitrogens then quaternizes slowly, and the fourth nitrogen resists quaternization even in boiling alcohol. Peek & Hill (137) made a study of the mutual influence of electrostatic fields in the series of dicarboxylic acids ranging from succinic to tetradecanedioic, using Speakman's (163) method. The solvent was methanol-water, 20:80 by weight, chosen to give sufficient solubility with the higher acids. Their experimental results are in agreement with the Kirkwood-Westheimer theory (104, 193). Using a hydrogen electrode in 60 per cent methanol, Everett & Wynne-Jones (49) measured the dissociation of the ammonium and the methylammonium ion at 10° intervals between 0 and 40°C. and present a thermodynamic analysis of their data. Measurements on di- and trimethylammonium ion were made at an ionic strength of 0.1.

In addition to dissociating into carboxyl ion and hydrogen ion, organic acids may dimerize with the formation of hydrogen bonds. Barton & Kraus (9) were able to account for their cryoscopic measurements in benzene on benzoic acid and a series of substituted benzoic acid, using the hypothesis of dimerization. Likewise, Katchalsky and co-workers (99) showed that dimerization in aqueous solutions of carboxylic acids was necessary to account for observed conductance data.

In strongly acid media, such as sulfuric acid and oleums, aromatic nitro-compounds accept a proton, giving the ion  $Ar \cdot NO \cdot OH^+$  [Brand, Horning & Thornley (29)]. The ionization could be followed spectrometrically because the proton addition shifts the principal absorption band by 6 to 9000 wave numbers towards lower frequencies, and simultaneously doubles the absorption coefficient. As the sulfur trioxide content of the oleum is increased, there appears a steady increase in concentration of the ionic species; for mono-nitrocompounds, the reaction reaches practical completion. The influence of polar substituents on the acidity constant is in moderately good agreement with electrostatic theory (104).

Davis & Hetzer (39) compared the base strengths of 1,3-di-*o*-tolyl-, diphenyl-, and triphenyl-guanidine and of triethylamine in benzene, using bromophthalein magenta E simultaneously as an acid and as an indicator, and followed the course of the reaction spectrophotometrically. The color and reaction sequence is: (a)  $B + HA$  (yellow)  $\rightleftharpoons BH^+ A^-$  (magenta); (b)

$\text{BH}^+\text{A}^- + \text{B} \rightleftharpoons (\text{BHB})^+ \text{A}^-$  (blue). The constants found for the first reaction (which measures the tendency of the bases to form salts with the acid indicator in benzene) do not run at all parallel to the ionic dissociation constants of the bases in water. The systems studied represent an excellent example of the hazards of attempting to extrapolate behavior in water to other solvents. The authors present an analysis of their findings in terms of solvation (187) and strain (30).

#### KINETICS

Complex ion formation has long been an intriguing subject for research; the field has been considerably broadened by a recent note by Bjerrum & Poulsen (23). The familiar reaction between nickel and dimethylglyoxime, for example, is a rapid reaction under ordinary conditions and hardly the subject for kinetic work. In methanol at  $-75^\circ\text{C}$ ., however, the reaction is slow enough to follow colorimetrically. The authors list a number of other reactions which have been observed qualitatively, and promise a more detailed publication dealing with the mechanism of complex formation. Their preliminary conclusion is that "most complex-reactions are instantaneous at room temperature due to a high value of the frequency factor rather than a low activation energy."

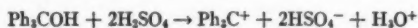
Radiotracers are beginning to find application in the fields of kinetics and mechanism of complex formation. By using labelled carbon in cyanide ion, Adamson, Welker & Wright (1) investigated the exchange of the cyanide unit between free cyanide ion and the hexacyanomanganate ion. They conclude that a hepta-coordinated transition state containing six cyanide units and one water molecule controls the exchange, the rate of which is independent of cyanide ion concentration, but proportional to cyanomanganate concentration.

In studying the kinetics of the reaction between dodecyl bromide and thiosulfate ion (88) Kolthoff & Johnson (105) discovered a new type of solubilization. Dodecylammonium bromide is readily soluble in water, as a normal 1-1 electrolyte below  $0.013\text{ }M$  and as a micellar electrolyte above this critical concentration, while dodecylammonium thiosulfate is relatively insoluble, having a solubility product of only  $3.8 \times 10^{-9}$ . Below  $0.013\text{ }M$ , the bromide acts in the normal way as a strong electrolyte with a common ion to suppress the solubility of the thiosulfate; above the critical concentration, however, counter ions of the micelles can exchange with ions in the free solvent. Hence the nearby ion atmosphere of the micelles contains both bromide and thiosulfate ions, and the attendant depletion of the bulk of the solution of thiosulfate ion increases the solubility of the dodecylammonium thiosulfate. The increase is linear in bromide ion concentration above the critical.

The following is a catalogue of kinetic work in which the role of electrolytes appears to be especially important, either as reagent or catalyst: (17)

decomposition of nitramide in the presence of sodium, calcium, barium, or zinc salts of various carboxylic acids; (138) oxidation of iodine by periodate in acetate buffer; (6) oxidation of tetrathionate by iodine; (52, 180) reaction between ferric and iodide ions; (161) oxidation of thiosulfate by peroxydisulfate, catalyzed by cupric ion; (176) reaction of sulfite ion with cystine and with dithiodiglycolic acid by polarographic methods; (162) oxidation of thiosulfate by selenious acid; (87) reduction of thallic ion by ferrous ion; (15) the competing reactions in the system ferrous and ferric ions, quinone and hydroquinone; (192) oxidation of manganous ion to permanganate by periodate; and (50) oxidation of ferrous ion by persulfate. The last mentioned reaction is of interest in polymer chemistry; the influence of various emulsifying agents was therefore also investigated.

Triphenylmethyl chloride in the nitroalkanes presents a rather unusual situation. Bentley, Evans & Halpern (19) find that the absorption spectrum of  $\text{Ph}_3\text{CCl}$  in nitromethane in the range 360 to 480  $\mu$  closely resembles that of the corresponding carbinol in concentrated sulfuric acid, where previous workers (71, 72) have shown that the reaction



is substantially complete. They therefore conclude that there is an equilibrium between neutral  $\text{Ph}_3\text{CCl}$  molecules and the ionic isomer  $\text{Ph}_3\text{C}^+\cdot\text{Cl}^-$  in nitromethane. But the ratio of  $[\text{PhC}^+]^2$  to total solute varies by an order of magnitude for only a five-fold change of concentration; hence the ion pair  $\text{Ph}_3\text{C}^+\cdot\text{Cl}^-$  does not dissociate into free ions, despite the high dielectric constant of the solvent. The potential energy of the ion pair as a function of the carbon-chlorine internuclear distance would therefore appear to have a minimum, instead of being monotone decreasing.

#### IRREVERSIBLE PROCESSES

Extrapolation of conductance data for associated electrolytes has been simplified by Daggett's (38) compilation of the Shedlovsky (159) function in tabular form. This function differs from that of Fuoss & Kraus (54, 58) in that an empirical approximation is made for higher terms in the Onsager conductance equation. The choice between these functions is not decisive (59) because they give coinciding values for  $K$  when association is considerable, and different values only in the range where the association hypothesis itself is somewhat insecure. In this range, one difference (which may eventually turn out to be significant) between the functions is observed: for a group of salts of related structure, the Shedlovsky  $K$ 's vary less than one might expect with structure parameters.

Spedding, Porter & Wright (164) have measured the conductance of aqueous solutions of the chlorides of lanthanum, cerium, praeosodymium, neodymium, samarium, europium, erbium, and ytterbium at 25°C., over the concentration range from  $4 \times 10^{-4}$  to 0.1  $N$ . The lanthanum data agree

perfectly with previous precision work (91, 120). Beginning with neodymium, the limiting conductances of the rare earth ions decrease; this parallels the decrease of crystallographic radius and shows that hydration is largely determinative in the mobility of cations in water. Dawson and co-workers (40) report conductances of the barium salts of methane-, ethane-, and propanesulfonic acids in water at 0, 20, and 25°C. The difference of 9.2 between the conductance of the methanesulfonate ion and the ethanesulfonate is considerably larger than the difference of 5.1 between the acetate and propionate ions, although both pairs differ by only one methylene group. Also, the high conductance (48.9) of the methanesulfonate ion compared to that of the acetate ion (40.9) is striking. Taft & Welch (181) have measured the conductance of sodium oxalate, malonate, and succinate in water at 0, 25 and 50°C. over the range from 0.02 to 1.9 *N*. Here again a large difference in limiting conductance appears for the first methylene: at 25°,  $\lambda$  (oxalate) is 74.1 and  $\lambda$  (malonate) is 63.5. Conductance, density, and relative viscosity at 95°C. have been determined by Campbell & Kartzmark (32) for concentrated (up to 15 *M*) solutions of silver and ammonium nitrates.

Denney & Monk (43) find evidence for ion association in aqueous thiosulfate solutions, both by solubility and by conductance measurements. Magnesium, manganese, calcium, cobalt, and nickel thiosulfates have *K*'s about twice as large as the sulfates; since the conductance of the thiosulfate ion (87.4) is larger than that of the sulfate ion (80.0), the effective electrostatic and hydrodynamic radii of these ions are exactly reversed. Association with zinc and cadmium ion is much stronger than with the ions mentioned above, indicating that more than electrostatic forces are involved here. The metals copper and silver which precede zinc and cadmium in atomic number complex very strongly with thiosulfate (the former after reduction to cuprous ion, of course). In the series magnesium, calcium, strontium, barium thiosulfates, the electrostatic and hydrodynamic radii are in the same sequence, as would be expected on the assumption of hydrated cations. Colman-Porter & Monk (37) have used the solubility and conductance methods to determine the extent of ion association in strontium iodate and hydroxide solutions, for comparison with previous data (121, 194) on calcium and barium. The association to  $\text{MIO}_3^+$  is in the sequence corresponding to hydrated cations (92). Monk (126, 127) has also studied a variety of poly-metaphosphates, in which considerable ion association occurs.

A different type of association, namely, micelle formation, takes place in aqueous solutions of salts containing long alkyl chains in the anion or cation. Tartar and co-workers (116) have made an extensive conductimetric study of magnesium hexane-, octane-, decane-, and dodecane-sulfonates at several temperatures, in continuation of their program of research on colloidal electrolytes. The critical micelle concentration (where the conductance curve abruptly becomes very steep) moves to lower concentrations in a regular fashion as the number of carbon atoms in the anion increases. In the range of concentrations below the critical, where the salts are essentially

behaving as strong electrolytes, the approach to the Onsager slope is usually from above.

Bigich (22) has measured the conductance of the ammonium chloride-aluminum bromide complex in nitrobenzene at  $10^\circ$  intervals between 20 and  $50^\circ\text{C}$ . The specific conductance-concentration curve has a broad maximum around 25 to 30 per cent solute, but a monotone rising function is obtained by multiplying by the viscosity. Dawson (41) studied dimethylformamide solutions of silver perchlorate, magnesium, zinc, and cadmium bromides and magnesium and zinc iodides over the temperature range from  $-50$ – $20^\circ\text{C}$ . Phosphorus oxychloride was used as the solvent in a series of solubility and conductance measurements by Gutmann (69); as suggested by the dielectric constant, considerable ion association occurs. Gorenbein & Kriss (66) studied the conductance of the system antimony tribromide-aluminum tribromide-arsenic tribromide. Molten mercuric bromide (m.p.  $238.5^\circ\text{C}$ .) was used as a solvent for a variety of electrolytes in a conductimetric study by Jander & Brodersen (86). Other systems of fused salts include silver chloride-silver nitrate (169) and binary mixtures of magnesium chloride with other chlorides (82). Jones & Worsfold (90) used conductimetric methods to follow the conversion of benzyl chloride into benzyl iodide by the reaction with potassium iodide in acetone. The method is much faster than the conventional analytical methods, and promises to be useful in this type of reactions.

Carrelli & Rescigno (33) have designed a simple resonance method of obtaining high frequency data: a cell is placed in an *LC* circuit, which is coupled to a seven megacycle oscillator and a rectifier circuit. The system is calibrated by using acetone-water mixtures in the cell in parallel with known resistances; then electrolytic solutions are placed in the cell, and a match between the resonance curve and the calibration is sought. Electrolytic solutes lower the dielectric constant below that of water; a shallow minimum (decrement about five units) appears around  $10^{-3}$  *N*. No significant difference was found (34) between the conductance at audio-frequencies and at 14 megacycles for potassium chloride in water to which glycerine and similar substances were added to produce relative viscosities up to nearly four; evidently the macroscopic viscosity still describes the resistance of a solvent to ionic motion even at quite high frequencies. These authors also report some preliminary measurements on weak electrolytes (ammonium hydroxide and acetic acid) at seven megacycles (35).

Transference numbers of lanthanum, cerium, praeosodymium, neodymium, samarium, europium, erbium, and ytterbium in aqueous solutions at  $25^\circ\text{C}$ . were determined by Spedding, Porter & Wright (165), using the method of moving boundaries (119). The concentration range covered was 0.007 to 0.1 *N*; the transference numbers for all the cations (except ytterbium) were linear in the square root of concentration. As Longworth & MacInnes (120) found for the case of lanthanum, the slopes of the lines are, however, steeper than the theoretical limit in the working range of con-



centration. The transference numbers of the first five rare earth cations are practically identical; beyond samarium, there is a decrease with increasing atomic number. The paper also contains formulas for computing the densities of aqueous solutions of the rare earth chlorides at 25°C. up to 0.1 *N*. Dutt & Gupta (46) measured transference numbers of cerium and lanthanum as thiosulfates; in order to account for the concentration dependence, they postulate the formation of a complex ion which contains three thiosulfate ions and one rare earth ion. Brady's (28) analytical boundary method was used by Spiro & Parton (168) in a study of aqueous silver nitrate solutions. In this method, the indicator ion is the leading ion; initially, two electrolytes with a common ion are placed in a cell and separated by a porous diaphragm. After passage of a known number of coulombs, the amount of the test ion which has migrated through the disc is determined by analysis. The authors conclude that the method will give three figure accuracy in the range around 0.1 *N* solutions. Kortum & Weller (106) used the Hittorf method in an investigation of lithium picrate in ethanol-water mixtures. They conclude that the picrate ion is unsolvated, because its effective radius was found to be independent of solvent composition. Lithium ion, on the other hand, is solvated, and preferentially by water; the fraction of water in the solvate shell of the cation was shown to be higher than in the bulk of the solvent.

Diffusion constants can be determined rapidly and with fair precision by a new method proposed by Wall, Grieger & Childers (190). A porous disc is soaked in a solution of the substance under investigation and then its loss of weight with time on standing in pure solvent is followed. Integration of the diffusion equation is given for the cases of sealed and open edges on the disc; in principle, the method should give absolute values of diffusion coefficients, but certain mathematical approximations make it more convenient to use it as a relative method. Stokes (171) has used the data of Gosting (67) and of Harned & Nuttal (75, 76) on the diffusion of potassium chloride to compute a table of integral diffusion coefficients as a function of concentration up to 3.9 *M*. This table will make future work with the diaphragm cell (124, 170) considerably more convenient. The diaphragm cell was used by Nielsen, Adamson & Cobble (129) to study self-diffusion in solutions of sodium chloride and of sodium sulfate. Their analytical method was based on the use of the radioactive isotopes: Na<sup>24</sup>, Na<sup>22</sup>, S<sup>35</sup>, and Cl<sup>36</sup>. Robinson & Chia (144) used the diaphragm cell to extend the available data (74) on calcium chloride to higher concentrations. Stokes' (170) technique was used. The integral diffusion constant of calcium chloride has a shallow minimum at about 0.35 *M*. Burkell & Spinks (31) have measured self-diffusion in aqueous solutions of sodium dihydrogen phosphate, using radioactive P<sup>32</sup>. Wang (191) has measured the diffusion of tracer amounts of radioactive sodium ion in potassium chloride solutions and proposes the logical term "tracer-diffusion" to distinguish this type of experiment from "self-diffusion" in which a radioactive tracer diffuses through a solution of

its own inactive isotopes. The corresponding diffusion constant is a complicated function of the concentration of potassium chloride, with a minimum and a maximum. Wang discusses his results in terms of ionic solvation and emphasizes the fact that continuum theory (131) cannot be expected to account for data in the range of concentrations covered by his experiments.

Soret coefficients in 0.1 *N* lithium, sodium, and potassium chloride solutions were measured by Alexander (3) who used a glass frit to separate the hot and cold parts of the system. A dependence of the Soret coefficient on temperature was observed, but the author pointed out the fact that the effect might have its origin in the frit. Tanner (184) measured the Soret coefficients in dilute solutions of potassium and barium chlorides, over the temperature interval 25 to 35°C.

The transmission and absorption of sound waves through electrolytic solutions has been a fairly active field. Barnartt (7) derived a limiting relationship between velocity of sound and concentration, using the ionic atmosphere model. Barrett & Beyer (8) showed that it is in general not permissible to assume that the ultrasonic absorption coefficient is composed additively of terms arising separately from solvent and solute. Krishnamurty (110) showed that the conductance of an electrolytic solution is decreased during the transmission of an ultrasonic beam. Tamm (182, 183) compared absorption of various salt types over a very wide range of frequencies. He found significant absorption for the valence type 2-2 and higher; an observed frequency dispersion of the effect indicates that a relaxation process is involved. Absorption coefficients in solutions of magnesium, copper, cadmium, nickel, and zinc were measured by an improved method by van Itterbeek & Verhaegen (84). A number of salts were investigated by means of an ultrasonic interferometer by Yasunaga, Sasaki & Fujiwara (150, 195, 196); the data were used to compute the volume of water of hydration per mole of solute. Yeager & Hovorka have investigated the effect of sound waves on the behavior of the hydrogen electrode (197).

#### POLYELECTROLYTES

Work on polyelectrolytes for the period 1938 to 1951 was reviewed by Doty & Ehrlich (44) and approximately the same period was covered by Fuoss (57). Bauman, Anderson & Wheaton (14) stressed the usefulness of polyelectrolytes in interpreting the behavior of ion exchange resins, which are from the point of view of the polymer chemist cross-linked polyelectrolytes. In this connection, three recent papers should be mentioned: Glueckauf (64) and Duncan (45) considered the equilibria between resin and solution by treating the resin phase as a concentrated electrolytic solution, and Juda and co-workers (93) introduced the concept of ion association in their treatment of the resin phase. Polyelectrolytes also play an important role in biochemical processes; it is hoped that other reviewers will cover this aspect of the subject, because we shall discuss here only the physical chemistry of polyelectrolytes.



Pals & Hermans (133, 134, 135) have made a detailed study of the sodium salts of pectin and of carboxymethyl cellulose. The first paper describes a series of careful determinations of viscosity in the presence of sodium chloride, the concentration of the latter chosen to give approximately constant ionic environment. Two practical experimental findings should be mentioned; the authors find (a) that no correction need be made for the difference between the surface tension of solution and solvent, and (b) that the apparent viscosity depends on the rate of shear, especially in the range of low concentrations. Reduced viscosities  $\eta_{sp}/c$  were plotted against polymer concentration  $c$  at constant ionic strength; the resulting straight lines were extrapolated to  $c=0$  in order to obtain intrinsic viscosities. The latter were then plotted against reciprocal square root of ionic strength [cf., Fuoss & Strauss Fig. 4 (60)] in order to obtain the quantity corresponding to the hypothetical limit of infinite charge density in the environment. The figures obtained were approximately proportional to the degree of polymerization, but the Stokes radius calculated seems unreasonably small. As the authors point out, this is a familiar discrepancy between theory and experiment in the application of the Brinkman, Debye-Bueche, or Kirkwood-Riseman theories. In the limit of low added salt concentrations, the carbohydrate chain appears to be fully extended; dimensions calculated by application of Simha's formula (160) for ellipsoidal particles are in a reasonable range of values for the molecular length. The second paper of this series reports the determination of the molecular weights of the test materials by means of osmotic pressure measurements, and the third paper is an important discussion of potentiometric titrations. In the case of polybasic acids of high molecular weight, successive dissociations become more difficult as the internal field increases, but simultaneously, the accompanying expansion of the coil due to increasing intramolecular repulsion weakens the field. The mutual interactions of these various effects have been the subject of considerable theoretical work. Neither the early theories of Katchalsky & Gillis (100) nor of Hermans & Overbeek (80) lead to a satisfactory correlation of experimental titration curves and molecular dimensions. Pals & Hermans mention, however, that the present theories do not consider sufficiently the Donnan equilibrium between the inside and the outside of the coils, the fluctuations of molecular dimensions nor possible effects of polyelectrolyte on the activity coefficients of the simple electrolytes present. Katchalsky (98) has made a brief report of an improved treatment of the thermodynamics of polyelectrolytes, but full details are not yet available.

Schaeffgen & Trivisonno (153, 154) have measured the viscosities of a series of polyamides in formic and sulfuric acids. Ordinarily, one thinks of the polyamides as neutral polymers, but in strongly acidic solvents, they become electrolytically charged, as shown by their strongly curved reduced viscosity-concentration curves. They also show the characteristic sensitivity to added simple electrolytes which is exhibited by more familiar polyelectrolytes; in formic acid, addition of formate or bromide ion reduces

the viscosity, and in sulfuric acid, the self-ionization of the solvent is sufficient to repress to a considerable extent the high viscosity. In the latter solvent, a small amount of water completely represses the polyelectrolyte behavior, because water is a strong base in sulfuric acid. Tetra- and octa-chain polymers (152) were investigated in formic acid in addition to linear polycapromides; as expected from their structure, the former gave lower viscosities under comparable conditions as a consequence of the restraints placed on expansion of these molecules by the central multifunctional unit. The viscosity data did not conform to the Fuoss equation (56); instead of a square root term in the denominator, the authors found that the following function fits their results:

$$\eta_{sp}/c = A/(1 + Bc) + D$$

In the above equation,  $D$  is very nearly equal to the value of the intrinsic viscosity of the polymers in concentrated sulfuric acid, where polyelectrolyte behavior is repressed and the compounds behave like neutral polymers. The results indicate that the polyamides uncoil in formic acid, but not to the extent exhibited by very highly charged polyelectrolytes such as the polyvinylpyridinium salts (57); the dependence on  $1/(1+Bc)$  rather than on  $1/(1+Bc^{1/2})$  is presumably also a consequence of the different charge density.

The viscosity of polyelectrolytes represents a peculiarly vexing problem: despite the wealth of data in the literature (some contributed by the author of this review) no one really knows what he is talking about. This embarrassing situation is due to the non-Newtonian behavior of polyelectrolyte solutions. Many of the data in the literature have been measured in Ostwald (or modified Ostwald) viscometers in which the rate of shear varies during the flow time, and in any case, the average rate of shear is never reported: hence these data all contain the unknown effects of a hidden variable. Some observers have used a Bingham viscometer (or the equivalent) in which rate of flow can be varied; their measurements show that apparent viscosities may vary by as much as a factor of two or more over a pressure range from 20 to 200 g./cm<sup>2</sup>. Akkerman, Pals & Hermans (2) have studied sodium carboxymethylcellulose, and Fuoss & Strauss (174) poly-N-butyl vinylpyridinium bromide: their results on these quite different systems agree on the significant conclusion that the shear sensitivity increases with increasing dilution. In other words, just where one would like to be most certain of results is where the unknown effects are most pronounced! Theoretical approaches (111, 139, 140) have so far been of no help: those available deal only with neutral polymers, and even here, a sharp conflict with experiment appears. The theory calls for a quadratic dependence of apparent viscosity on velocity gradient, and at least two (51, 70) empirical analyses over the usual range of variables shows a linear dependence. The theoretical situation for polyelectrolytes certainly will be more complicated.

Strauss & Fuoss (174) have extended the empirical analysis (70) to the case of polyelectrolytes: they find that the shear dependence increases with dilution about as fast as the reduced viscosity itself increases. They summarize their results by the one constant equation

$$\eta_{sp}/c = z_{\infty}(1 - \alpha z_{\infty}\beta)$$

where  $z_{\infty}$  is the reduced viscosity at concentration  $c$  extrapolated linearly to infinite flow time (zero rate of shear) and  $\beta$  is the (average) velocity gradient. Concentration dependence is implicit in the appearance of  $z_{\infty}$  in the coefficient of  $\beta$ . The result is, however, only empirical, and there is no assurance whatsoever that the linear extrapolation made by these authors to  $z_{\infty}$  is justified. Possibly the eventual theoretical function will turn out to be something like  $A + B(1 + k\beta^2)^{1/2}$  which is quadratic in  $\beta$  for very low values of  $\beta$ , but imitates a linear function with deceptive fidelity when  $k\beta^2 \gg 1$ .

Strauss and co-workers (85, 115, 173, 175) have opened a new field of research in which conventional colloid chemistry and polyelectrolyte chemistry are combined: by quaternizing polyvinylpyridine with *n*-dodecyl bromide, for example, a polyelectrolyte is formed in which the chained cations are typical surface-active groups. Strauss has introduced the name "polysoaps" for compounds of this general structure. The long alkyl side groups form micelles and thereby reduce the viscosity of polysoap solutions to values smaller than those for polyvinylpyridinium salts with small N-alkyl groups. The polysoaps solubilize hydrocarbons more efficiently on a gram for gram basis than the corresponding monosoaps, and no critical concentration appears: the local concentration in each individual polymer coil is always above critical, regardless of the bulk concentration. When aliphatic hydrocarbon is solubilized by the polysoap, the viscosity decreases; the authors interpret this result as a contraction of the polysoap coil brought about by the enhanced van der Waals attraction energy which results from addition of more hydrocarbon into the coil. With aromatic solubilizates, on the other hand, an increase of viscosity appears initially, followed by a maximum with subsequent decrease to the saturation value. Strauss attributes this effect, which contrasts markedly with the reaction with aliphatic hydrocarbons, to an interaction between polysoap molecules which is in turn a consequence of a change of configuration produced by solution of the aromatic hydrocarbon in the polar region of the polysoap. The solubility of benzene in 2 per cent polysoap solution is 10 times that of *n*-octane, so clearly the interaction between polysoap and hydrocarbon is greater for aromatics. The dependence of the maximum rise in viscosity on concentration of polysoap establishes the necessity of postulating interaction between polysoap molecules. Evidence for association to aggregates was found in a polysoap with about equal numbers of N-ethyl and N-*n*-dodecyl groups; reproducible solubilization and viscosity appeared after prolonged heating which dissociated the aggregates.

A number of other papers on solution properties of polyelectrolytes have appeared: lack of space precludes a detailed discussion of the results. We shall therefore limit the remainder of this review essentially to an abstract of the Abstracts. Hermans (79) has measured the osmotic pressure of cellulose xanthate gels. Basu & Gupta (11) find that sodium carboxymethyl cellulose exhibits the viscosity behavior characteristic of polyelectrolytes, and made the significant observation that the conductance of mixtures of sodium chloride and the polycarboxylate was less than the sum of the individual conductances. Seiyama (158) obtained a similar result with mixtures of sodium alginate and simple electrolytes. Other properties of sodium alginate are reported by Seiyama [specific volume (157)], Endo [osmotic pressure and viscosity (48)], and by Harkness & Wassermann [viscosity in the presence of simple electrolytes (73)]. Viscosities of the sodium salt of gum arabic were measured by Basu and co-workers (10). A fairly detailed study of sodium cellulose-glycollate has been made by Kagawa and co-workers (95, 96) and by Inagaki & Noguchi (83).

# SOLUTIONS OF ELECTROLYTES

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## SOLUTIONS OF NONELECTROLYTES<sup>1</sup>

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If one should desire to describe the progress made in the field of solutions of nonelectrolytes during the year 1952, one would probably have to use the word "consolidation." It has been a year in which the various methods of theoretical approach have been correlated, in which more attention has been paid to the minor but still important aspects, and one in which explanations of certain phenomena have been offered. It is indeed satisfying to have Guggenheim's "Mixtures" (1) published in this year. This book brings together in one place all the contributions of Guggenheim and his co-workers to this field.

Greater attention is given in this review to liquid solutions although a general survey of all types of solutions has been attempted. A review of this nature is certainly subjective but an effort towards objectivity has been made. It is hoped that not too many important papers have been neglected or overlooked.

*Theoretical.*—The exact theory of the liquid state and of solutions can be developed in principle by the methods of statistical mechanics but the mathematical difficulties are enormous. Other methods making use of models have therefore been used, notably the free-volume theory. In 1950, Kirkwood (2) showed that the free-volume theory of Lennard-Jones & Devonshire (3) was a first approximation to the more exact theory. Salsburg & Kirkwood (4) have now extended this study to multicomponent systems by using the method of moments in the treatment of the order-disorder problem. They have shown that the retention of the first moment gives an approximation of the partition function used by Prigogine and his co-workers. They also give an approximation to retaining the third moment. The calculation of the thermodynamic functions from the first moment approximation is discussed. While it is possible to compute the higher moments, the numerical calculations become extensive and have not been done. In this correlation between the two theories, however, it has been assumed that the cells postulated in the free-volume theory are of the same size and further the problem of the communal entropy has not been treated.

Prigogine & Mathot (5) have extended the work of Prigogine & Garikian (6), applying the cell or free-volume method to solutions. They have assumed that the molecules are spherical in shape, that the distance of maximum interaction between the different type of pairs is approximately the same, and that there is random mixing. The potential energy between two molecules  $i$  and  $j$  is assumed to be given by

$$\epsilon_{ij}(r) = \epsilon_{ij}^* [(r_{ij}^*/r)^{12} - 2(r_{ij}^*/r)^6]. \quad 1.$$

<sup>1</sup> The survey of the literature pertaining to this review was concluded in December, 1952.

However, Prigogine & Garikian (7) have shown that the results are largely insensitive to the force law of the mean field and consequently Prigogine & Mathot have also made use of the harmonic oscillator model and the smoothed potential model (potential curve with vertical sides and flat bottom). It is further assumed that the Gibbs and Helmholtz free energies are approximately the same. An equation of state is obtained for each of the three cases on the assumption that  $PV/kT$  approximates zero. Thus, the volume depends upon the temperature and composition but is not a function of the pressure. It is considered that the process of mixing takes place at a constant but small pressure. The volume of mixing and the excess free energy, energy and entropy have only been estimated using equation 1 but have been calculated for the two other models because the numerical calculations are simpler in these two cases. The results for the two models are similar except for an additional term, which depends upon the change of the vibration frequency with concentration, in the harmonic oscillator model. As a consequence, only the smoothed potential model is discussed in detail. In all three cases it is found that both the energy of mixing at constant pressure (approximately the heat of mixing) and the excess entropy of mixing depend upon the volume of mixing and, in the smooth potential model, the excess entropy of mixing is directly proportional to the volume of mixing. This result is similar to that which Scatchard (8) obtained in determining the difference in the thermodynamics functions on mixing at constant pressure and on mixing at constant volume. Lacher, Buck & Parry (9) also have pointed out the apparent identity of sign of the volume of mixing and the excess entropy of mixing at constant pressure. The theory of conformal solutions of Longuet-Higgins (10) agrees with the first-order terms of the present theory but it does not give the higher-orders. The detailed results of this theory for the smooth potential model are indeed of interest. When the interaction term for the unlike molecules,  $\epsilon_{AB}^*$ , is taken to be the geometrical mean of the interaction terms for the like molecules, the energy of mixing is positive and the volume of mixing is negative. If it is taken as the arithmetical mean, the energy of mixing is small and negative and the volume of mixing is also negative. When  $\epsilon_{AA}^*$  and  $\epsilon_{BB}^*$  are taken as approximately equal but  $\epsilon_{AB}^*$  is much smaller than either, both the energy of mixing and the volume of mixing are positive, but, if  $\epsilon_{AB}^*$  is much larger, both the energy and volume of mixing are negative as would be expected. When  $\epsilon_{AA}^*$  and  $\epsilon_{AB}^*$  are of the same order but  $\epsilon_{BB}^*$  is much larger, the volume of mixing becomes fairly unsymmetrical although positive but may be both negative and positive while the energy of mixing will be more symmetrical and positive. If  $\epsilon_{BB}^*$  and  $\epsilon_{AB}^*$  are of the same order but  $\epsilon_{AA}^*$  is much smaller, the volume of mixing is negative and may be unsymmetrical while the energy of mixing will also be negative but practically symmetrical.

Rowlinson (11) has made a similar study to that of Prigogine & Mathot (5) but has made use of the quasi-chemical approximation of Guggenheim which eliminates the assumption of random mixing. The energy of inter-

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action between two molecules is assumed to be given as a function of a distance variable,  $d/r$ , where  $d$  is a distance constant for all species. The Lennard-Jones form of this function using the 6-12 law is used only where necessary. The free-volume of a molecule in a cell is given as

$$v = \int_{\text{cell}} e^{-E(R)/kT} 4\pi R^2 dR \quad 2.$$

where  $R$  is the distance of the molecule from its lattice site and  $E(R)$  is its energy at this distance above that at the site. The free-volume is a function of the composition. The discussion concerns the evaluation or estimation of four parameters,  $(j_0)_A$ ,  $(j_0)_B$ ,  $(j_1)_A$ ,  $(j_1)_B$ . The assumption that  $(j_0)_A = J_A$ ,  $(j_0)_B = J_B$  and  $(j_1)_A = (j_1)_B = (J_A J_B)^{1/2}$  yields the equations of strictly regular solutions as defined by Guggenheim. In these equations  $J_A$  and  $J_B$  are the free volumes for the pure substances. The assumption that  $(j_1)_A = (j_1)_B = J_{AB}$  gives the same approximation obtained by Ono (12). Here  $J_{AB}$  is the free volume of an  $A$  molecule surrounded by  $B$  molecules which is identical to that of a  $B$  molecule surrounded by  $A$  molecules. A third approximation is given by assuming  $(j_0)_A = (j_1)_A = J_A(\bar{\omega}_A)$  and  $(j_0)_B = (j_1)_B = J_B(\bar{\omega}_B)$  where  $J_A(\omega_A)$  is the free volume of an  $A$  molecule with  $\omega_A$  neighbors of species  $B$  and  $(1-\omega_A)$  of species  $A$  and  $\bar{\omega}$  is the average value of  $\omega$  at the given composition. This approximation is essentially that of Prigogine & Garikian (6) but they further assumed that  $\bar{\omega}$  equaled the mole fraction. The equation giving  $J_A(\omega_A)$  explicitly as a function of  $\omega_A$  has been developed and a fourth, and probably the most accurate, approximation is made by determining  $j_0$  and  $j_1$  for both  $A$  and  $B$  from the tangent of the curve of  $J(\omega)$  at  $\bar{\omega}$ . This tangent will vary with the composition. In each of the last three approximations, terms in addition to those of the strictly regular solutions are obtained which depend upon the ratio of the interaction energy between the unlike molecules to the geometrical mean of the interaction energies between the like molecules. The point is made that these additional terms are important and that this ratio is not unity. The explanation given by Simons & Dunlap (13) and by Simons & Mausteller (14) for their results on the  $n$ -pentane- $n$ -perfluoropentane and  $n$ -butane- $n$ -perfluorobutane systems in terms of anomalous repulsive forces seems to be an attempt to account for the fact that this ratio is not unity. The general relationships for the volume of mixing are given and it is further shown that this theory agrees with the theory of conformational solutions which is independent of the cell model. As a result confidence can be placed in the free-volume theory.

Prigogine, Mathot-Sarolea, & Van Hove (15) have investigated the combinatory factor in regular solutions and have obtained an improvement on the quasi-chemical approximation by adding a parameter chosen to fit the perfectly ordered cases.

Prigogine & Marechal (16) have extended the work of Prigogine and his co-workers on the surface tension of binary solutions to the case where one molecule occupies  $r$  sites and the other only one site. They have made use

of the Flory-Huggins method and as a first approximation showed that the surface tension is additive in respect to the volume fractions. Marechal (17) has determined the surface tension of solutions of diphenyl, diphenyl acetylene, and dibenzyl in benzene and of 1,8-diphenyl octane in benzene. These measurements are in good agreement with the theoretical results of Prigogine and his co-workers (18, 19). The paper by Prigogine & Saraga (20) who have applied the cell model to the calculation of the surface-tension of a pure liquid may be mentioned here.

One of the most difficult problems that still needs to be attacked is the theoretical development of the equations for solutions containing molecules whose force fields are not symmetric. Barker (21, 22) has made one attack on this problem using the cell model in which the different types of molecules may occupy different numbers of sites. The mathematical treatment is based on the quasi-chemical approximation. It is assumed that the surface of a molecule is divided into several contact points, each of which may have a specific energy of interaction with the neighboring part of the surface of another molecule. With a judicious choice of parameters the thermodynamic functions of the methanol-benzene and methanol-carbon tetrachloride systems are calculated and show a remarkable agreement with the experimental results (23). However, only a qualitative agreement is obtained for the ethanol-chloroform system (24).

Tompa (25) has derived equations for the athermal entropy of mixing of polymer solutions occupying more than singly connected sets of sites. The results agree with those of Guggenheim for linear polymers and of Huggins for spherical molecules.

**Complexes.**—The interest in complex formation in solutions has continued in the past year. Andrews & Keefer (26) have studied the ultraviolet absorption spectra of iodine with mesitylene, durene, pentamethyl-, hexamethyl-, and hexaethylbenzene and of iodine monochloride with mesitylene, durene, pentamethyl-, hexamethyl-, hexaethyl-, ethyl-, isopropyl-, and *t*-butylbenzene. The equilibrium constants of the 1:1 complexes have been calculated and those of benzene, toluene, and xylenes with these halogens have been redetermined. All measurements were made in carbon tetrachloride solutions. The equilibrium constants for the methylbenzenes increase in the same order as that reported by McCaulay & Lien (27). However, the xylene-iodine monochloride complex formed by the *para* isomer appears to be the most stable rather than the least stable of the three xylenes. Ethyl substitution appears to increase the equilibrium constant to about the same extent as does methyl substitution but hexaethylbenzene forms very weak complexes which is explained in terms of steric effects.

Ketelaar & van de Stolpe (28) have reported the ultraviolet spectra of solutions of iodine with diisobutylene, *cis*-dichloroethene, trichloroethene and tetrachloroethene in *n*-hexane and calculated the equilibrium constants for the complex formations. The values of these constants decrease in the

order given above. Andrews & Keefer (29) have made similar studies of iodine with cyclohexene, 1-bromo-1-propene, *cis*-dichloroethene and *trans*-dichloroethene at 25°. The wavelength of the maximum absorption for these solutions ranges from 2620–3020 Å. There is good agreement between the two sets of data where comparison is possible. The values of the equilibrium constants for these olefinic compounds are of the same order as for aromatic compounds and again chlorination tends to decrease the stability of the complex. The equilibrium constant for the *trans*-dichloroethene is smaller than for the *cis*-complex. The heat of formation of the complex is estimated to be less than one kcal. per mole except for diisobutylene where it is greater than one kcal. per mole.

The equilibrium constants for the formation of complexes between iodine and dioxane in carbon tetrachloride and in *n*-hexane at several temperatures have been determined from the ultraviolet absorption spectra by Ketelaar, *et al.* (30). The equilibrium constant for the formation of the complex at 25° is 9.1 in carbon tetrachloride solutions and 9.3 in the hexane solutions. The change of enthalpy for the formation of the complex is  $-3500 \pm 200$  cal. per mole and the change of entropy is  $-7.3$  cal. per deg. mole.

The absorption spectra of iodine in propene, *cis*-2-butene, *trans*-2-butene, 1,3-butadiene and 2-methyl-1,3-butadiene, either pure or dissolved in propane, have been determined by Freed & Sancier (31) from 77° to 230°K. Again evidence is obtained of a 1:1 complex between the iodine and the olefines. In some cases an irreversible reaction occurs at the higher temperatures decolorizing the iodine solutions. The heats of formation of the addition compound vary from 200 to 500 cal. per mole.

Ham (32) has determined the equilibrium constants of iodine with diethyl ether and *t*-butanol at  $21.5 \pm 0.5^\circ$  from the spectra of solutions of these substances in *n*-heptane.

Landauer & McConnell (33) have determined the absorption spectra of solutions of aniline with *m*-dinitrobenzene, *p*-dinitrobenzene, and *s*-trinitrobenzene in chloroform solutions at approximately 22°. They have also calculated the equilibrium constants for the formation of the 1:1 complexes and have found evidences for the existence of 1:2 complexes. The use of chloroform may be questionable since there may be strong interaction between the chloroform and the aromatic molecules or with the nitro or amino groups.

The shift in the vibrational frequency of the OD band of methanol-*d* in chloro, bromo, and methyl substituted benzenes and the heat of mixing at 25° of chloroform with these same compounds has been determined by Tamres (34). A linear relationship is obtained between the heat of mixing at half mole fraction and the shift of the vibrational frequency. Methyl substitution causes an increase shift of the band and a larger heat of mixing in reference to benzene and chloro or bromo substitution results in a decreased effect. The position of the OD band when the methanol-*d* is dissolved in carbon tetrachloride is taken as the reference. While this choice may be

satisfactory for reference purposes, there is to be expected a shift of the OD band in this solution in comparison to that when the methanol is in the vapor state. It is claimed that a 1:1 complex is formed between chloroform and the aromatic compounds presumably on the fact that the heat of mixing has a maximum at half mole fraction. This, however, is not sufficient evidence for complex formation.

While the subject of this review is primarily on nonelectrolytic solutions, a discussion of complexes with aromatic and olefinic compounds is not complete without mentioning other types. Hepner, Trueblood & Lucas (35) have investigated the coordination of aqueous silver ion with 1-butene, *cis*-2-butene, *trans*-2-butene and 2-methylpropene by a distribution method. Also Trueblood & Lucas (36) have made similar studies with ethylene and propene. In both cases the results are explained on the basis of the formation of a 1:1 complex. The solubilities of toluene in aqueous silver perchlorate solutions have been determined and the ultraviolet spectra of certain of these solutions have been investigated by Keefer & Andrews (37). Again the results of these studies indicate the formation of a 1:1 complex and possibly a 2:1 silver ion-toluene complex.

The solubility of hydrogen chloride at  $-78.51^\circ$  in dilute solutions of aromatic compounds in toluene and in *n*-heptane has been measured by Brown & Brady (38). The aromatic compounds are halo and methyl substituted benzenes. The solubility is discussed in terms of complex formation and the basic properties of the aromatic nuclei.

Ham, Platt & McConnell (39) have investigated the spectra of benzene-iodine and benzene-bromine solutions in the wavelength range 2350–3500 Å. In both cases a new absorption band was found at 2600 Å. This band may be due to the  $^1A_{1g} - ^1B_{2u}$  electronic transition in benzene or possibly to the  $^1A_{1g} - ^3E_u$  transition.

The evidence of complexes of the halogens, silver ion, methanol, and hydrogen chloride with aromatic and olefinic compounds is rather strong as indicated by the results discussed above. However, there is one note of discordance. Ham, Rees & Walsh (40) have determined the infrared spectra of saturated solutions of iodine in benzene (1 part benzene and 5 parts carbon tetrachloride), ether and pyridine from 2.5–25 $\mu$ . The spectra of the benzene and ether solutions are identical within experimental error, to that obtained when no iodine is present and no detectable broadening is observed. Pyridine forms a crystalline complex with iodine and the formation of such a complex in solution is observed in the spectra. It is therefore concluded that no complex is formed with benzene or ether. Identical conclusions are drawn by the same authors (41) from the infrared spectra of solutions of iodine in mesitylene. This conclusion is somewhat substantiated by the work of Taufen, Murray & Cleveland (42) who studied the Raman spectra of olefinic compounds and benzene in the presence of silver ion. In each case relatively large shifts of the olefinic double-bond frequency were observed with smaller frequency shifts in some of the carbon-hydrogen vibrations.



The two Raman-active carbon-carbon stretching vibrations of benzene also were shifted.

Brown & Brady (38) in their work have differentiated between the type of complexes discussed in this review and those formed between aromatic nuclei and such combinations of substances as hydrogen chloride with aluminum chloride. The first type are called  $\pi$ -complexes and the second  $\sigma$ -complexes. These latter complexes are considered beyond the scope of this review. Mulliken (43) has developed a rather complete classification of complexes based on his charge-transfer concept.

*Intermolecular forces.*—The contribution of London to our knowledge of intermolecular forces has been of inestimable value; however, our knowledge of the intermolecular forces certainly is not complete. As an example it does not necessarily explain the formation of the complexes discussed in the previous section.

Mulliken (44) has developed a general quantum mechanical theory which will account for the formation of molecular compounds ranging from loose complexes to stable compounds. This theory also accounts for the intense absorption bands observed in the ultraviolet region due to the presence of complexes. In agreement with Brachmann (45), Mulliken claims that the complex as a whole is responsible for the absorption and not one of its constituents. This theory assumes that an electron may transfer from a donor to an acceptor. The ground state of any molecular complex is written as  $\psi_N = a\psi_0 + b\psi_1 + \dots$  where  $\psi_0$  is the "no-bond" wave function of the component parts and  $\psi_1$  is a "dative" wave function corresponding to the transfer of an electron from the donor component of the complex to the acceptor. In such a case there is a resonance energy stabilizing the complex. An essential requirement, however, is that  $\psi_1$  shall be of the same group-theory species as  $\psi_0$ . This means usually that  $\psi_1$  must be of the same spin type as  $\psi_0$  and of the same orbital species under the group-theoretical classification corresponding to the over-all symmetry of the complex as a whole. There is an excited state whose wave function is  $\psi_E = a^*\psi_1 - b^*\psi_0 + \dots$  with  $a^*$  and  $b^*$  approximately equal to  $a$  and  $b$ , respectively. In loose molecular compounds it is expected that  $a^2 \gg b^2$  which means that  $\psi_N$  has nearly pure no-bond character and  $\psi_E$  nearly pure ionic character. The spectrum associated with this transition is called an intermolecular charge-transfer spectrum. For more stable complexes  $a$  and  $b$  should be more nearly equal with  $b$  becoming probably greater than  $a$ . The structure of the benzene-iodine complex is assumed to be one in which the axis of the iodine molecule is parallel to the plane of the benzene molecule and its center on the six-fold axis of the benzene. However, other structures might be feasible. The charge-transfer forces are strongly orienting in character because of the symmetry restrictions and consequently the structure of the complexes may not be those conceived in terms of London's forces. Mulliken further discusses silver complexes, complexes of the  $BX_3 \cdot NR_3$  type and also Lewis acids and bases. He also points out that these charge-transfer forces may

be important in pure substances, as in pure benzene, and share with the London dispersion forces in accounting for the over-all observed attractive forces.

Shuler (46) has recently discussed the free-electron model for  $\pi$ -molecular complexes. These complexes are those formed between  $\pi$ -electron acceptors and  $\pi$ -electron donors where both partners are linear or planar conjugated systems. In this theory it is assumed that the  $\pi$ -electrons of conjugated molecules move as a free-electron gas in the potential field of the molecule. It can be closely correlated with the charge-transfer process of Mulliken.

A few other contributions to the study of intermolecular forces have been published during the past year. Brooks (47) has shown that the commonly used perturbation method of estimating these forces leads to divergent results. The divergent intermolecular force series is shown to be asymptotic to the true molecular interaction. The divergence is removed in an approximate way. The method gives results for the interaction between the proton and hydrogen atom and between helium atoms in good agreement with exact calculations or experiment. Coulson & Davies (48) have studied the dispersion forces between conjugated molecules using molecular orbitals. They conclude that the inverse sixth law is obeyed only at very large distances of the order of twice the molecular size and that the attractive force is of different form at other distances, that at large distances the energy varies with the fifth power of the length of each molecule, that the dispersion forces show marked directional properties, and that for molecules of sufficient length the  $\pi$ -electron forces become more important than the  $\sigma$ -electron forces (with six carbon atoms the  $\pi$  effect is four times the  $\sigma$  effect). Kirkwood & Shumaker (49) considered another type of electrostatic interaction between protein molecules which arises from fluctuations in charge and charge-distribution associated fluctuations in the number and configuration of the protons bound to the molecules. The fluctuating electric field of each molecule alters the distribution of fluctuations in the charge and constellation of the mobile protons in such a manner as to produce at the isoionic points a long range attractive force with a potential diminishing asymptotically as the inverse square of the distance in the absence of screening by the statistical space charge of an electrolytic environment.

Thomaes (50) has calculated the dispersion forces between carbon tetrafluoride molecules and silicon hexafluoride molecules on the basis of localizing the interaction forces in the fluoride atoms rather than the center of the molecule itself. Good agreement is obtained with the force law determined by MacCormack & Schneider (51) from the second virial coefficient. Rowlinson (52) has made a similar study of the intermolecular forces of the same molecules.

Hornig & Hirschfelder (53) have obtained an expression for the London dispersion forces between unlike molecules in terms of the resonant frequencies and the polarizabilities of the two molecular species. Each molecule

is represented by a three-dimensional isotropic harmonic oscillator and the energy of interaction is calculated by the second order perturbation method.

The intermolecular potentials between carbon dioxide molecules and between carbon dioxide and nitrous oxide molecules have been calculated by Amdur, Ross & Mason (54) from the diffusion coefficients in the range  $-78^\circ$  to  $90^\circ$  using the Lennard-Jones & Devonshire form of the potential. It was not possible, however, to obtain a single set of parameters which could satisfactorily reproduce all of the gaseous properties. The failure may be due either to the inadequacy of the potential form or the importance of inelastic collisions.

*Liquid-liquid mixtures.*—The change of the Gibbs free energy on mixing at constant pressure has been expressed mostly as

$$\Delta F^M = RT \sum_i n_i \ln x_i + \Delta F_z^E \quad 3.$$

where  $x_j$  is the mole fraction of the  $j$ th component and  $\Delta F_z^E$  is the excess Gibbs free energy defined by this equation.<sup>2</sup> With the introduction of the Flory-Huggins theory the free energy of mixing may also be expressed by the equation

$$\Delta F^M = RT \sum_i n_i \ln z_i + \Delta F_v^E \quad 4.$$

where  $z_j$  is the volume fraction of the  $j$ th component. The quantity,  $\Delta F_v^E$ , may be called the excess free energy on the volume fraction basis. Obviously the two excess free energies are not identical except in the case that the molal volumes of the components are identical. If the heating of mixing,  $\Delta H^M$ , is determined from the temperature dependence of the excess free energies, slightly different values may be obtained depending on whether equation 3 or 4 is used. Thus, from equation 3

$$\Delta H^M = \left( \frac{\partial \Delta F_z^E / T}{\partial 1/T} \right)_{P,n} \quad 5.$$

and from equation 4

$$\Delta H^M = \left( \frac{\partial \Delta F_v^E / T}{\partial 1/T} \right)_{P,n} + R \sum_i n_i \left( \frac{\partial \ln z_i}{\partial 1/T} \right)_{P,n} \quad 6.$$

$$= \left( \frac{\partial \Delta F_z^E / T}{\partial 1/T} \right)_{P,n} - RT^2 \sum_i n_i \left( \alpha_i^0 - \sum_i z_i \alpha_i^0 \right) \quad 7.$$

where  $\alpha_i^0$  is the coefficient of expansion of the  $j$ th component. This last term is usually quite small and in many cases may be neglected. On the other hand  $z_j$  may be considered as independent of the temperature and pressure, in which case it would be determined at some arbitrary temperature and pressure. Similar considerations are applicable to both the change of entropy and volume on mixing at constant pressure. Thus we have from equation 3

<sup>2</sup> This symbol and similar ones, such as  $\Delta H_z^M$  and  $\Delta S_z^E$ , should not be confused with those used by Scatchard which denote molal quantities.

$$\Delta S^M = -R \sum_j n_j \ln x_j + \Delta S_z^E \quad 8$$

and

$$\Delta V^M = \left( \frac{\partial \Delta F_z^E}{\partial P} \right)_{T,n} \quad 9.$$

while we obtain from equation 4

$$\Delta S^M = -R \sum_j n_j \ln z_j - RT \sum_j n_j \left( \alpha_j^0 - \sum_i z_i \alpha_i^0 \right) + \Delta S_z^E \quad 10.$$

and

$$\Delta V^M = \left( \frac{\partial \Delta F_z^E}{\partial P} \right)_{T,n} + RT \sum_j n_j \left( \beta_j^0 - \sum_i n_i \beta_i^0 \right). \quad 11.$$

When the changes of the Helmholtz free energy, energy and entropy for the process of mixing at constant volume are considered, the question of the dependence of the volume fraction on temperature again enters. The volume of the components may be taken at a fixed pressure, usually one atmosphere, and at various temperatures in which case the volume fraction will be a function of the temperature. On the other hand the volume of the components may be taken at a given temperature and pressure and used as an independent variable. In this case the volume fraction would be independent of the temperature. The difference between these two cases may be expressed in terms of processes of mixing. In the first case the process of mixing is done at constant volume, but the volume would vary with the temperature; in the second case the process of mixing is again at constant volume with the volume held constant independent of the temperature. It is this latter case that is usually treated theoretically.

The questions as to the suitability of these equations, especially equations 4, 7, and 10, to reproduce the experimental data, the dependence of  $\Delta H^M$  on either the mole fraction or the volume fraction and the agreement of theoretical results with the observed arise. The differences in the changes of the thermodynamic functions for the process of mixing at constant pressure and for the process of mixing at constant volume should not be neglected. Scatchard and co-workers (55, 56, 57) [see also the work of Wood and co-workers (58, 59, 60)] have shown that the difference between the Gibbs free energy of mixing at constant pressure and the Helmholtz free energy of mixing at constant volume is negligibly small while the difference between the heat of mixing at constant pressure and the energy of mixing at constant volume and that between the two excess entropies of mixing are quite marked.

Hildebrand & Scott (61) have studied the partial molal entropy of mixing of iodine in carbon tetrachloride and *n*-perfluoroheptane. They have used the equation

$$\bar{S}_2 - S_2^0 = R \left( \frac{\partial \ln a_2}{\partial \ln x_2} \right)_T \left( \frac{\partial \ln a_2}{\partial \ln T} \right)_{\mu_1, \mu_2^0} \quad 12.$$

in which  $(\partial \ln a_2 / \partial \ln T)_{\mu_2 = \mu_2^s}$  is the change of the logarithm of the activity of iodine in respect to the logarithm of temperature along the saturation curve. Hildebrand (62) has shown this relation to be almost linear except in concentrated solutions. They have estimated the change of the activity with mole fraction at constant temperature according to the simple solution theory making use of their solubility parameters. The values thus calculated are compared with those calculated according to the equation.

$$\Delta S^M = -R \sum_i n_i \ln z_i \quad 13.$$

(compare equation 10). The difference between the partial molal entropy of iodine determined by this equation and the ideal partial molal entropy is only 0.19 cal. per degree for the carbon tetrachloride solutions and 1.2 cal. per degree for the *n*-perfluoroheptane solutions. However, a discrepancy between these calculated values and those obtained from the experimental data still exists. The effect of the volume of mixing on the entropy of mixing accounts approximately for this discrepancy.

In order to check the theory of Guggenheim and his co-workers (1) under more exact conditions than the use of equation 4, Everett & Penny (63) have studied the vapor pressures of solutions of benzene and diphenyl, diphenylmethane, and dibenzyl over the temperature range 25° to 75°. The deviations from ideal solutions for the first system are positive and are negative for the last two. The theoretical values calculated on the assumptions that one molecule occupies two sites in a lattice while the other molecule occupies only one and that the number of nearest neighbors is six are in agreement with the experimental results provided that the energy of mixing is considered. The quantity, *Nw*, in calories per mole is found to be independent of temperature and is 153 for the diphenyl solutions, 63 for the diphenylmethane solutions, and 70.5 for the dibenzyl solutions. Systematic deviations which are attributed to the entropy are observed in the more concentrated solutions of diphenyl. This comparison with the theory would be more effective if the volume of mixing had been taken into account. After this paper of Everett & Penny appeared Marechal (64) reported the volumes of mixing and the surface tensions of solutions of benzene and diphenyl, dibenzyl, diphenylacetylene and 1,8-diphenyloctane. The volume of mixing of the first three solutions is negative in agreement with the prediction of Prigogine & Mathot (5) while that of the last solution is almost zero. The vapor pressures of diphenylacetylene-benzene solutions from 40° to 60° are also reported and are found to be in agreement with the theory of Guggenheim with *Nw* being 119 cal. per mole. Here again, however, the volume of mixing has not been included.

Scatchard, *et al.* (65) have measured the heats of mixing of methanol-carbon tetrachloride, methanol-benzene, carbon tetrachloride-benzene, carbon tetrachloride-cyclohexane, benzene-cyclohexane, *n*-hexane-*n*-hexadecane, methanol-carbon tetrachloride-benzene, and carbon tetrachloride-benzene-cyclohexane systems at 20°. The heats of mixing of the three binary

systems of benzene, carbon tetrachloride, and cyclohexane determined from the vapor pressure measurements of Scatchard, Wood & Mochel (55, 56, 57) are in good agreement with these calorimetric values. Scatchard & Ticknor (23) have recalculated the heats of mixing of the methanol-benzene and methanol-carbon tetrachloride systems from the vapor pressure data of Scatchard, Wood & Mochel (66, 67) using a more correct approximation to the equation of state of the vapor phase. On this basis the two sets of data are in essential agreement. This result emphasizes the necessity of using correct equations of state of the vapor phase in determining the heats and entropies of mixing from vapor pressure data. The heat of mixing of the *n*-hexane-*n*-hexadecane system was used in conjunction with the free energy determined by Brønsted & Koefoed (68) in order to determine the entropy of mixing. The values thus obtained are approximately equal to those calculated by the Flory-Huggins theory, although it has not been possible to make accurate use of the volume of mixing. It is shown that the enthalpy of the ternary mixtures can be calculated from that of the three binary systems only if the polar component is treated differently from the nonpolar components. The experimental heats of mixing of the nonpolar mixtures are at least as symmetrical on the volume fraction basis as on the mole fraction basis.

The heats of mixing of the three binary systems formed from the three components, carbon tetrachloride, chloroform, and methylene chloride, and for the systems benzene-carbon tetrachloride and benzene-ethylene dichloride have been reported by Cheesman & Whitaker (69). These heats of mixing are all positive. It is claimed that the heat of mixing is more symmetrical on the mole fraction scale than on the volume fraction scale. The simple theory of Scatchard and Hildebrand gives the energy of mixing at constant volume as being symmetrical in terms of the volume fraction. The difference in the symmetry in the heats of mixing on the two scales appears to be rather small for all the systems studied except for the benzene-ethylene dichloride system. However, the volume of mixing has not been considered. It would seem then that no definite decision as to the suitability of the two scales can be made. It is admitted however that at least to a first approximation the volume of mixing would be symmetrical on either the mole fraction or volume fraction scales. The benzene-ethylene dichloride system is asymmetric on both composition scales. At approximately half-mole fraction the heat of mixing of the benzene-carbon tetrachloride system is reported as 23.5 cal. per mole at 17.80° and 26 cal. per mole at 24.70° in comparison to the value of 31 cal. per mole at 20° reported by Scatchard *et al.* (65). It is pointed out that the heat of mixing cannot be calculated accurately using Hildebrand's solubility parameters. The discrepancy primarily lies in the assumption that the term for the interaction between the unlike molecules is the geometrical mean of those for the like molecules.

The determination of the properties of systems without consideration of

any theory is also important. Many such papers have been published this year. In one instance Wood & Gray (70) have studied the effect of volume and temperature on the energy and excess entropy of mixing at constant volume for the three binary systems using carbon tetrachloride, benzene, and cyclohexane. In particular they have calculated these quantities at 70° but at the molal volume at 25° and one atmosphere pressure from those at the molal volume at 70° and one atmosphere pressure by means of the Tait equation. Within the accuracy of these calculations it appears that these functions are only slowly varying functions of the temperature but are definitely dependent upon the volume. Preliminary calculations lead one to expect that this result is also true for the pure substances.

The equilibrium vapor pressures and compositions of the two phases for the hydrogen peroxide-water system have been measured by Scatchard, Kavanagh & Ticknor (71) at 60°, 75°, and 90° and for approximately equimolar mixtures at 45° and 105°. A simple theory in which it is assumed that the variation with composition of the cohesive energy of these mixtures is due entirely to hydrogen bonds and that the energy of a hydrogen bond is independent of the nature of the molecules involved or of other reactions of either molecule involved provides a fair approximation to the dependence in composition and leads to reasonable values for the extent of association and for the strength of the hydrogen bond. The Flory-Huggins theory is used as a basis of these calculations. The densities of these mixtures at 0°, 10°, 25°, 50°, and 96° have been reported by Easton, Mitchel & Wynn Jones (72). The results are in good agreement with those of Huckaba & Keyes (73).

Scatchard & Ticknor (23) have measured the vapor-liquid equilibrium of the ternary system, methanol-carbon tetrachloride-benzene and have been able to express the thermodynamic functions by an equation containing terms involving the mole fractions of two of the components only and no term involving the mole fractions of all three components.

Brown (74) has measured the liquid-vapor equilibria of benzene-*n*-heptane, *n*-hexane-chlorobenzene, and cyclohexane-nitrobenzene systems. The vapor pressures and equilibrium compositions of mixtures of *n*-butane and *n*-perfluorobutane have been measured by Simons & Mausteller (14).

Probably one of the most interesting systems to study is that of He<sup>3</sup> and He<sup>4</sup> although the experimental difficulties are so great that accurate measurements have not been obtained to date. Daunt & Heer (75) have reported probably the most accurate measurements which indicate positive deviations from Raoult's law, both below and above the lambda point. The results, however, are not sufficiently accurate to differentiate between the theory of Heer & Daunt (76) in which the solution is regarded as a mixture of model liquids which are represented by Fermi-Dirac and Bose-Einstein statistics and that of de Boer & Gorter (77).

Desseigne & Belliott (78) have reported the index of refraction at 20° and the liquid-vapor equilibria at one atmosphere pressure of nitromethane-



methanol systems. Brändstrom & Schotte (79) have measured the densities and boiling points of binary mixtures of acetone with 1,2-dichloro-, 1,1,2-trichloro-, and 1,1,1,2-tetrachloroethane. The volume of mixing for the first system is positive while it is negative for the last two systems.

The volume relations of the first six primary alcohols, *n*-octanol and *n*-decanol in benzene, heptane, and cyclohexane have been studied extensively by Staveley & Spice (80). Their results might be, but not definitely, explained on the assumption of the polymerization of the alcohols to trimers. The densities at 25° of the binary mixtures of water with dioxane, acetone, and pyridine and of the ethanol-pyridine system have been determined by Griffiths (81).

Babb & Drickamer (82) have made turbidity measurements on binary systems of methanol with *n*-pentane, *i*-pentane, and *n*-hexane. They discuss the possibility of determining the thermodynamic properties of solutions from these measurements.

Rotariu, Haycock & Hildebrand (83) have determined the solubility of water in liquid phosphorus and Rotariu, Fraga & Hildebrand (84) have measured its solubility in *n*-perfluoroheptane. They have calculated the solubility parameter of water using the equation

$$-\ln z_2 = z_1 \left( 1 - \frac{V_2}{V_1} \right) + \frac{V_2 z_1^2}{RT} (\delta_2 - \delta_1)^2.$$

The value of this quantity ranges from 26.2 for phosphorus to 23.8 for *n*-perfluoroheptane. The very small variation is indeed surprising and makes it possible to calculate the solubility of water in a nonpolar liquid with some confidence. However, in such use these solubility parameters have become empirical rather than retaining their original meaning. It is the opinion of this reviewer that this trend is unfortunate.

*Solid-liquid mixtures.*—The simple theory of Hildebrand and Scatchard predicts an enhanced solubility of a solid solute in a mixture of two solvents when the cohesive energy density of the solid lies between those of the two solvents. Gordon & Scott (85) have studied this phenomenon for the system phenanthrene-cyclohexane-methylene iodide using equation 3 with the further relation that

$$\Delta F_s^E = \sum_{ij} z_i z_j V (\delta_i - \delta_j)^2.$$

The enhanced solubility is observed. However, there was no composition of the solvents in which the ideal solubility was observed as would be predicted by the theory. The phase diagram of the methylene iodide-cyclohexane system has been determined.

Simons & Linevsky (86) have measured the solubility of naphthalene, *p*-nitrotoluene and hexachloroethane in diperfluorobutyl ether, (C<sub>4</sub>F<sub>9</sub>)<sub>2</sub>O, and triperfluoropentylamine, (C<sub>5</sub>F<sub>7</sub>)<sub>3</sub>N, at 25° and 35°.

*Gas-liquid mixtures.*—Gjaldback (87) has determined the solubility of



hydrogen in *n*-perfluoroheptane and carbon disulfide, of oxygen in *n*-heptane and carbon disulfide, and of carbon monoxide in *n*-heptane, *n*-perfluoroheptane, benzene, and carbon disulfide. He has found good agreement with the equation

$$-\log x_2 = -\log x_2^s + \log \bar{V}_2/V_1 + 0.434 \left(1 - \frac{\bar{V}_2}{V_1}\right) + \frac{\bar{V}_2(\delta_1 - \delta_2)^2}{4.575T}$$

which is based on equation 4. The values for the solubility parameters are 5.7 for oxygen, 5.8 for carbon monoxide and 5.1 for hydrogen. The partial molal volumes are 52 ml. for carbon monoxide, 46 ml. for oxygen, and 37 ml. for hydrogen.

Robin & Vodar (88) have continued their studies of the solubility of liquids in compressed gases. They have studied the systems of methanol-hydrogen, methanol-methane, methanol-carbon dioxide, iodine-carbon dioxide, carbon disulfide-carbon dioxide, carbon disulfide-nitrogen, and carbon disulfide-hydrogen and found the logarithm of the molality to be linear to the density in agreement with the theory of Lennard-Jones & Devonshire; not as good agreement was found for the benzene-nitrogen and the benzene-hydrogen systems. For the systems of water in methane, carbon dioxide, nitrogen, and hydrogen the logarithm of the molality is a non-linear function of the density.

Kretschmer & Wiebe (89) have measured the solubilities of propane, *n*-butane, and isobutane in methanol and isopropanol at pressures up to one atmosphere and at temperatures between 0° and 50° and have calculated the thermodynamic functions of these systems.

*Metallic solutions.*—Kleppa (90) has discussed the determination of the thermodynamic functions from freezing point diagrams. The method is restricted to simple eutectic diagrams with a steep liquidus curve displaced toward one extreme in composition. It is assumed that both the heat of mixing and entropy of mixing are independent of the temperature and that the heat of mixing is symmetrical either in the mole fractions or volume fractions. Thermodynamic data are obtained for the binary systems copper-bismuth, copper-lead, and copper-thallium. No choice can be made between the two ways of expressing the heat of mixing.

Kleppa (91) has determined the thermodynamic properties of zinc-bismuth and zinc-lead systems in the liquid state from electromotive force measurements. Trumbore, Wallace & Craig (92) have used electrochemical methods to determine the heats, free energies, and entropies of formation of solid alloys of magnesium and cadmium. The excess entropy is positive in cadmium rich solutions and also exhibits a pronounced minimum at approximately half-mole fraction. Buck, Wallace & Rulon (93) have determined the heats of formation of the same alloys at 25° calorimetrically. The liquid ternary system of bismuth-cadmium-tin has been studied by electromotive force methods by Mellgren (94) and the thermodynamic functions of this

system have been calculated using the methods of Darken (95). Halla & Herdy (96) have determined the activities in the liquid ternary system, sodium-mercury-lead, by electro-motive force methods. The activity of copper in its alloys with gold over the whole range of composition from 401° to 848° has been measured by Chiche (97) and the entropy of cuprous oxide has been calculated.

The influence of sulfur on the solubility and activity coefficient of carbon in liquid iron has been studied by Kitchener, Bockris & Spratt (98).

Fournet (99) has studied theoretically the order-disorder modifications in copper-zinc alloys using the methods of Yvon (100) and obtained good agreement with their experimental results.

*Solutions of polymers.*—Stockmayer & Casassa (101) have made a study of the third virial coefficient in the expression for the osmotic pressure of a polymer in solution as a function of its concentration. The study is based on the theory of Flory & Krigbaum (102) but the integrand in the expression for the first virial coefficient is assumed to be a simple exponential with a choice of constants being made to make the best fit with the expression used by Flory & Krigbaum. It is necessary to evaluate one constant obtainable from intrinsic viscosity or light scattering measurements. The ratio of the third virial coefficient to the square of the second is less than 5/8 given by the hard sphere molecular model.

Krigbaum & Flory (103) have extended their theory and have obtained expressions for the osmotic pressure and turbidity of a dilute solution of two chemically dissimilar polymer species in a solvent. The results show that the expressions obtained on the basis of the quasi-crystalline lattice model are not valid for very dilute solutions except in special cases.

The phase equilibria of the diisobutyl ketone-polyisobutylene and cyclohexane-polystyrene systems have been studied by Shultz & Flory (104). The temperature-composition curves are similar in character to those calculated from thermodynamic theory but are broader and the critical volume fractions are approximately twice the predicted value. The linear relationship between the reciprocal consolute temperature and a function of the ratio of the molal volumes of polymer and solvent molecules is in accordance with the theory but the thermodynamic parameters calculated from the straight lines are at variance with those obtained by other methods. The phase diagram of the three component system consisting of cyclohexane and two polystyrenes exhibits similar deviations.

Guggenheim & McGlashan (105) have discussed a different extrapolation, based on a comparison of different solutes in the same solvent, for the determination of molecular weights of polymers from measurements of osmotic pressure.

The melting temperatures of solutions of polychlorotrifluoroethylene in toluene, mesitylene, *o*-chlorobenzotrifluoride have been measured by Bueche (106). Consistent values of the heat of fusion and the solubility

parameter of the polymer are obtained. Hall (107) has determined the solubility of the same polymer in cyclohexane, methylchloroform, carbon tetrachloride, *p*-xylene, toluene, benzene, mesitylene, the tetrachlorides of tin, titanium and germanium, boron trichloride, and cyclohexene. The thermodynamic quantities such as the solubility parameters and the heat of fusion of the polymer and the interaction parameters related to the entropy and enthalpy have been calculated. The estimation of the solubility in nonpolar liquids is discussed.

The solubility of polymethyl methacrylate and polyvinyl acetate has been measured in 16 solvents by Daoust & Rinfret (108) in order to determine which had the best solvent properties and proper index of refraction for use in light scattering measurements.

*Miscellaneous.*—Gilliland & Sullivan (109) have measured the fugacity of ethylene in nitrogen, hydrogen, and ethane. The fugacity of the ethylene was controlled by use of the solid compound which it forms with cuprous chloride. The temperature ranged from 0° to 40° and the pressure up to 4000 lbs. per sq. in. It is shown that the Lewis and Randall rule can be greatly in error for these mixtures. Several other rules for the determination of the fugacity of a component in a gas mixture are studied and a method based on using the partial molal logarithm of the fugacity of the mixture is recommended.

The second virial coefficients for the binary mixtures of hexane-chloroform, hexane-diethyl ether, and chloroform-diethyl ether have been reported by Fox & Lambert (110). The second virial coefficients of ethane, hexane, cyclohexane, benzene, ethylene, chloroform, diethyl ether, carbon tetrachloride, and triethylamine are also given.

The dielectric constants, densities, and indices of refraction of *tert*-butylchloride and methylcyanide in various solvents have been measured by Smith & Witten (111). The available theories do not adequately represent the differences between the dielectric constants of these compounds when they are in solution and in the vapor state. Similar studies on the polarizations and apparent dipole moments of 18 aliphatic and aromatic amines in non-polar solvents and those of 15 amines in the liquid state have been made by Cowley (112). The solvents used were hexane, cyclohexane, and benzene.

Stallard & Amis (113) have studied the water-dioxane system with respect to the index of refraction, the specific heats, the total and partial specific and molal heats of vaporization, and the absorption of dioxane by sulfuric acid.

Mention should be made of two symposia on phase equilibria published by the American Institute of Chemical Engineers as part of a symposium series of *Chemical Engineering Progress* (109, 114). A number of papers on various aspects of liquid-vapor equilibria and liquid-liquid equilibria are published in these two volumes.

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# ISOTOPES<sup>1</sup>

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## INTRODUCTION

The subject of isotopes touches on every field of chemistry, and it is not possible in a review of this kind to cover all phases of isotopic research or to avoid some duplication with other sections of this volume. This review, like the previous ones, covers the general field of the chemistry of isotopes and is chiefly concerned with differences in the thermodynamic properties of isotopes (energy, entropy, and free energy) and in their properties relating to chemical kinetics. Studies of isotope fractionation, which occurs in chemical processes both in the laboratory and in nature, are of considerable importance in increasing our understanding of chemical equilibrium, chemical kinetics, reaction mechanisms, and in unravelling the history of the earth. Studies of this kind have been reviewed. In addition, isotopic abundances and atomic masses fundamental to all isotope studies are subjects included in this review.

## ATOMIC MASS DETERMINATIONS

During the past few years there has been an increased emphasis on precision mass measurements, and much elaborate equipment is being designed for this purpose. This increased interest in precise mass determinations comes about because of the advances now being made in the theory of the nucleus and the need for more precise data. Precise atomic masses are required to check on the accuracy of total decay energies for nuclear transformations and to identify and measure quantitatively nuclear shell structure effects. Nuclear masses thus provide fundamental data with which any theory of nuclear forces must be reconciled.

A new instrument for precision mass measurements has been reported by Hipple & Sommer (1). This instrument is a crossed-field and time-of-flight mass spectrometer designed to have a resolution of one in 100,000.

Richards, Hayes & Goudsmit (2) have determined the masses of  $\text{Pb}^{208}$  and  $\text{Bi}^{209}$  by measuring the time of flight of their ions in a magnetic field. Their results are in reasonable agreement with the values derived from the disintegration data of Harvey (3). The fact that the difference in mass between  $\text{Bi}^{209}$  and  $\text{Pb}^{208}$  turns out to be 5 m.M.U. greater than unity, indicates a sharp increase in slope of the packing fraction curve. This agrees with the expectations since  $\text{Bi}^{209}$  has one proton more than the "magic number" 82.

During the year Duckworth (4) published a binding energy/nuclear mass

<sup>1</sup> The survey of the literature pertaining to this review was concluded in December, 1952.

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# ISOTOPES<sup>1</sup>

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## INTRODUCTION

The subject of isotopes touches on every field of chemistry, and it is not possible in a review of this kind to cover all phases of isotopic research or to avoid some duplication with other sections of this volume. This review, like the previous ones, covers the general field of the chemistry of isotopes and is chiefly concerned with differences in the thermodynamic properties of isotopes (energy, entropy, and free energy) and in their properties relating to chemical kinetics. Studies of isotope fractionation, which occurs in chemical processes both in the laboratory and in nature, are of considerable importance in increasing our understanding of chemical equilibrium, chemical kinetics, reaction mechanisms, and in unravelling the history of the earth. Studies of this kind have been reviewed. In addition, isotopic abundances and atomic masses fundamental to all isotope studies are subjects included in this review.

## ATOMIC MASS DETERMINATIONS

During the past few years there has been an increased emphasis on precision mass measurements, and much elaborate equipment is being designed for this purpose. This increased interest in precise mass determinations comes about because of the advances now being made in the theory of the nucleus and the need for more precise data. Precise atomic masses are required to check on the accuracy of total decay energies for nuclear transformations and to identify and measure quantitatively nuclear shell structure effects. Nuclear masses thus provide fundamental data with which any theory of nuclear forces must be reconciled.

A new instrument for precision mass measurements has been reported by Hipple & Sommer (1). This instrument is a crossed-field and time-of-flight mass spectrometer designed to have a resolution of one in 100,000.

Richards, Hayes & Goudsmit (2) have determined the masses of  $\text{Pb}^{208}$  and  $\text{Bi}^{209}$  by measuring the time of flight of their ions in a magnetic field. Their results are in reasonable agreement with the values derived from the disintegration data of Harvey (3). The fact that the difference in mass between  $\text{Bi}^{209}$  and  $\text{Pb}^{208}$  turns out to be 5 m.M.U. greater than unity, indicates a sharp increase in slope of the packing fraction curve. This agrees with the expectations since  $\text{Bi}^{209}$  has one proton more than the "magic number" 82.

During the year Duckworth (4) published a binding energy/nuclear mass

<sup>1</sup> The survey of the literature pertaining to this review was concluded in December, 1952.

curve based on mass spectrometric mass values obtained in his laboratory and mass values calculated from these using disintegration, transmutation, and microwave absorption data. Duckworth points out that this set of values is more likely to be internally consistent than one compounded from several sources, although recently reported values, chiefly from Professor Nier's group at Minnesota and Goudsmit's group at Brookhaven, are generally in agreement. The binding energy/nuclear mass curve plotted shows sudden changes in slope to occur at  $\text{Ni}^{62}$ ,  $\text{Sr}^{88}$ ,  $\text{Sn}^{120}$ ,  $\text{Ce}^{140}$ , and  $\text{Pb}^{208}$ , which are attributed to nuclear shell closure at proton numbers 28, 50, and 82, and at neutron numbers 50, 82, and 126; five features already well authenticated. His graph also shows fine structures which require further study and several unexplored regions.

A great deal of excellent data has appeared recently from Professor Nier's laboratory which indicate further fine structure in the binding energy curve. Using a double focussing mass spectrometer, described previously (5, 6), and measuring doublets involving hydrocarbon fragments, Collins, Nier & Johnson (7) have measured 27 atomic masses in the region from titanium to zinc. These are supplemented by their earlier data and nuclear energies to give the masses of 81 nuclides between mass numbers 31 and 70. A fit of their data to the semi-empirical mass formula of Wigner (8) shows up discontinuities in the binding energy surface, which they associate with nuclear shell closures at 20 and 28 neutrons and protons. From the same laboratory Halsted (9) reports atomic mass determinations for 42 stable nuclides in the region from Pd through Xe which, combined with nuclear reaction mass differences, provide a table of 74 mass values from mass 102 to 136. Again discontinuities in the binding energy surface reveal shell closure at 50 protons.

Stanford *et al.* (10) measured some new doublets involving  $\text{Pb}^{207}$ ,  $\text{Pb}^{208}$ ,  $\text{Th}^{232}$ ,  $\text{U}^{234}$ , and  $\text{U}^{238}$ . Since these masses are related to one another through known disintegration data, they were considered as a group, and the individual masses were adjusted to secure a mutually consistent set of values. The value obtained for  $\text{Pb}^{208}$  was in excellent agreement with that of Richards, Hayes & Goudsmit (2).

Johnson (11) has made an interesting study of some doublets involving the three isobars  $\text{V}^{50}$ ,  $\text{Cr}^{50}$ , and  $\text{Ti}^{50}$ . The odd-odd  $\text{V}^{50}$  nuclide with an abundance of 0.24 per cent was discovered several years ago by Hess & Inghram (12) and by Leland (13), and the question arises as to its stability in regard to  $\beta^+$  or  $\beta^-$  emission. Johnson compared the mass differences for the three doublets  $\text{C}_4\text{H}_2\text{-V}^{50}$ ,  $\text{C}_4\text{H}_2\text{-Ti}^{50}$ , and  $\text{C}_4\text{H}_2\text{-Cr}^{50}$ , measured with a double focussing mass spectrograph described previously (6). From the results it is apparent that ample energy is available for decay of  $\text{V}^{50}$  to either  $\text{Cr}^{50}$  or  $\text{Ti}^{50}$ . Failure to detect this activity must be attributed to a long half-life.

The discrepancy in the mass of  $\text{C}^{12}$  and the value of the important doublet  $\text{C}^{12}\text{H}_4\text{-O}^{16}$  mentioned in last year's review is still unresolved. Detailed accounts of many of the current problems connected with mass measurements

will soon be published in the *Proceedings of the Conference on Mass Spectroscopy in Washington, September, 1951* (14).

#### ISOTOPE ABUNDANCE RATIOS

*Instrumentation.*—The conventional mass spectrometry still retains its pre-eminence as regards speed and accuracy of analysis of stable isotopes. Mass spectrometry has been reviewed recently by Mayne (15), and many problems related to the subject are discussed in the *Proceedings of Conference on Mass Spectrometry, 1951* (14) soon to appear. The calibration of mass spectrometers with isotopic mixtures of accurately known composition, a method used extensively by Nier (16), eliminates many discrimination factors inherent in absolute abundance measurements. Also, very high precision comparative isotopic ratios are now possible, using the simultaneous collection principle first applied by Straus (17) in Dempster's laboratory and using a dual sample system described by McKinney *et al.* (18) which permits the rapid alternate introduction of the reference and unknown samples. Comparative ratios of the isotopes of the light elements can be determined within 0.02 per cent (18).

During the past two years schemes have been suggested for adjusting the resolution of an isotope ratio instrument. Berry & Rock (19) have used an ion optic method for varying the resolution, instead of adjustable slits. In general, low resolving power is required for the determination of comparative isotopic ratios with speed and high accuracy. However, if the resolving power can be increased by a slit adjustment, then mass doublets due to impurities can often be resolved. In this connection, the high resolution time-of-flight mass spectrometers of the type developed by Smith (20) would be useful to supplement conventional mass spectrometers. Leland (21) has utilized a secondary electron multiplier as a current pre-amplifier to obtain improved sensitivity. Mass spectrometers equipped with these amplifiers are being used in a number of laboratories for special isotopic ratio problems, such as the detection of rare isotopes, the analysis of extremely small samples and of solid substances of low ionization efficiency (14).

McNally (22) discusses new and improved mass analysis equipment in the fields of atomic spectroscopy, microwaves, and nuclear resonance and suggests that spectro isotopic methods may offer advantages such as speed. In this regard Milatz, Kluyver & Hardebol (23) report an accuracy of 20 per cent in the determination of the normal  $C^{13}/C^{12}$  ratio by an infrared absorption spectra method, which they hope can be improved to give 1 per cent accuracy. Studenbrocher and co-workers (24) have used the isotope spectrum shift in the 6707.8 resonance line of Li to determine  $Li^6/Li^7$  ratios. The ratios obtained were good to 6 per cent.

Mass spectrometric analysis of deuterium in hydrogen gas is usually complicated because of mass discrimination and exchange isotope effects. Friedman & Irsa (25) have found that a mixture of mono and deuterio ethane

formed by the action of zinc diethyl with water can be analysed in a mass spectrometer with a precision of 0.3 per cent.

*Isotope abundance ratios.*—The most recent table of relative isotope abundances of the elements was published in December, 1950, by Bainbridge & Nier (26). Few papers on absolute abundances of isotopes in nature have appeared since that time. Reuterswärd (27) has redetermined the isotopic abundance of  $K^{40}$ . Since this natural occurring radioactive isotope is supposed to have an important role in the thermal balance in the earth's crust and is the source of  $A^{40}$  in rocks and in the atmosphere, its abundance in nature is of particular interest. Reuterswärd used the ratio  $K^{39}/K^{41}$  as an internal standard to correct his  $K^{39}/K^{40}$  ratio for mass discrimination inherent in his instrument, the recent result of Nier being taken as correct for the former ratio. He obtained  $7900 \pm 40$  for the  $K^{39}/K^{40}$  ratio. This compares with  $7800 \pm 80$  obtained by Nier (28).

*Isotope abundance ratios and their variations.*—The isotopes of the light elements fractionate in geological and biological processes due to differences in their chemical properties. Since the principle of isotope fractionation is now fairly well understood, the isotope abundances that occur in natural substances are indicative of their past chemical history, and isotope geology has become a fascinating and fruitful field of investigation. In this connection, the oxygen isotopes have received a great deal of attention. The early work was encouraging since many of the differences in  $O^{18}$  abundances could be readily explained by theoretical principles (29, 30). In this regard oxygen is unique among the elements in that the seas provide a large reservoir of oxygen in which exchange processes can occur at a fairly constant  $O^{18}$  level of concentration. Oxygen isotope abundances are discussed in a recent review by Dole (30).

During the past year three interesting papers have appeared concerning the relative abundances of the oxygen isotopes in igneous, sedimentary, and metamorphic rocks. Baertschi (31) and Baertschi & Silverman (32) showed the existence of measurable variations in the isotopic composition of the silicate oxygen of the lithosphere. Silverman (33) has extended the work and has discussed the implications of these variations. Silverman found a total variation of 2.4 per cent in the  $O^{18}$  content of his silica samples. His analysis indicated that sediments are consistently higher in  $O^{18}$  than are the igneous rocks. This implies that the deposition of silica from solution is accompanied by enrichment of the heavy isotopes in the precipitated phase. In accord with this, diatomite deposits composed entirely of silica precipitated from solution have the highest abundance of  $O^{18}$ . From the  $O^{18}/O^{16}$  ratios in sea water and diatomite the equilibrium constant for the exchange reaction



may be estimated to be 1.03 at the temperature of this precipitation. Silica in other sedimentary deposits is found to be enriched to the extent to which

surface exchange has taken place between the silica fragments and water. Silverman has compared the  $O^{18}$  enrichment of Brazil quartz with that of diatomite, the two formation temperatures being estimated at  $140^{\circ}\text{C}$ . and  $15^{\circ}\text{C}$ . respectively. This gives two points on the temperature isotopic composition scale and a temperature coefficient of 0.0128 per cent per degree for the silica water exchange. In 1947 Urey predicted that the silica water exchange would have a temperature coefficient similar to that for the  $\text{CO}_3^{=}-\text{H}_2\text{O}$  system (34). The above result is in agreement with this prediction.

Experiments have also been carried out by Silverman to determine the abundances of the oxygen isotopes in igneous rocks, which presumably have not been altered by erosion processes. Since these rocks are formed at high temperatures, their oxygen isotope concentrations are expected to be uniform and to represent the primordial composition. Some nine samples investigated were found to be from 0.65 to 0.85 per cent enriched in  $O^{18}$  as compared to Hawaii sea water. On the same scale several meteorites were found to be 0.65 per cent enriched in the heavy isotope. The oxygen isotope ratios of meteorites, therefore, fall within the range assigned to the primordial composition of our planet. The extraction of oxygen from silicates in a chemical form suitable for oxygen isotope analysis has been a difficult problem. Baertschi & Schwander (35) have described a new method for obtaining oxygen from silicate rocks for isotope analysis. In this method CO produced from the reaction of silica with carbon at  $2000^{\circ}\text{C}$ . in a high vacuum resistance furnace is analysed with a conventional isotope ratio mass spectrometer. Their preliminary results show excellent reproducibility, and further interesting  $O^{18}$  data on silicate rocks can be expected.

Urey and his associates (36, 37) are continuing their investigations of the  $O^{18}$  exchange between carbonate ions in solution and water. The  $\text{CO}_3^{=}-\text{H}_2\text{O}$  temperature scale suggested by Urey depends on a small but measurable temperature coefficient for the exchange equilibrium of  $O^{18}$  between  $\text{CaCO}_3$  and  $\text{H}_2\text{O}$ . Marine organisms lay down their carbonaceous shells in equilibrium with the sea water, and their  $O^{18}$  content will be indicative of the temperature of the sea at the time of formation. This is the basis of the paleo temperature scale. The main limitation on the determination of paleo temperatures by this method is an insufficient knowledge of the isotopic abundance of  $O^{18}$  in the parent water. It appears that there is considerable variation in this through the oceans. To eliminate this difficulty Urey is attempting to develop a similar  $\text{PO}_4^{=}-\text{H}_2\text{O}$  thermometer. Since it has a different temperature coefficient for  $O^{18}$  fractionation from that of the  $\text{CO}_3^{=}-\text{H}_2\text{O}$  scale, a combination of the two scales will suffice to determine the temperature at which carbonates and phosphates are formed in the sea and will eliminate the uncertainty in the composition of the water.

In 1939 Nier & Gulbransen (38) showed that the  $\text{C}^{12}/\text{C}^{13}$  abundance ratio varied by from 5 to 6 per cent in natural materials. It was found that limestone was enriched and carbon of organic origin depleted in  $\text{C}^{13}$ . These results have been confirmed and extended by later work (39), which has

been reviewed by Rankama (40). For carbon there is no large reservoir of material of more or less constant  $C^{12}/C^{13}$  ratio to provide a base level from which isotopic variations in other carbon compounds can be reckoned like the sea for oxygen. For this reason it is more difficult to trace the isotopic fractionation found to known chemical processes for which isotopic fractionation can be predicted by theory. However, studies of carbon isotope fractionation in nature have continued and some interesting results have been obtained. Wickman & Ubisch (41) and Wickman, Blix & Ubisch (42) have investigated the  $C^{13}$  content of a large number of carbonate minerals, such as dolomites and magnesites, which presumably are derived from limestone. The results show that the carbonate minerals cover the same range of isotopic ratios as do the limestone and carbonates from which they are derived. Dolomites were found to be very uniform in isotopic content and to have a lower  $C^{12}/C^{13}$  ratio than the median value for limestone rocks. In general, they find that minerals formed by cation exchange such as dolomites are enriched in  $C^{13}$ . Baertschi (43) has investigated the  $C^{12}/C^{13}$  and  $O^{16}/O^{18}$  ratios of 150 carbonate rocks, including sedimentary limestone, metamorphic limestone, intrusive carbonatites, calcite crystals, and calcareous sinters. The isotopes of oxygen and carbon were found qualitatively to fractionate in the same way as might be expected. His results for metamorphic limestones show a widespread variety in their isotopic compositions ranging from the sedimentary limestone with a high  $C^{13}$  content to the carbonatites with low concentration of this isotope. The results suggest that studies of these variations in isotopic content of metamorphic carbonate rocks might yield valuable information on the distribution and migration paths of  $H_2O$  and  $CO_2$  during metamorphism.

Mars in Sweden (44) and Trofimov in Russia (45) have made systematic surveys of the  $C^{12}/C^{13}$  ratio in a large number of natural materials. Their comparative results in general confirm the earlier work of Nier. The absolute values of the  $C^{12}/C^{13}$  ratios reported by Trofimov are somewhat higher than corresponding values reported by Nier (39) and Wickman (42). Trofimov gives an average value of 90.0 for the  $C^{12}/C^{13}$  ratio for limestone as compared to a previous average of 89.3, which value about coincides with sea water carbonates. In 1950 Nier (46) redetermined the absolute  $C^{12}/C^{13}$  ratio for samples of limestone investigated in 1941. In this latter work he calibrated his mass spectrometer with standard mixtures of  $A^{38}$  and  $A^{40}$  prepared from pure samples of the separated isotopes, and his ratio of  $C^{12}/C^{13}$  is probably accurate to 0.3 per cent. Nier concludes that the errors in his earlier work did not exceed 0.5 per cent. This limestone analysed by Nier provides a standard of comparison for other workers. Wickman<sup>2</sup> recently compared the  $C^{12}/C^{13}$  ratio for his standard carbonate with the Nier analyzed limestone and concludes that all previous relative measurements of  $C^{12}/C^{13}$  ratio should be revised upward by about 0.3 per cent. This would bring the aver-

<sup>2</sup> Private communication through H. von Ubisch.

age value for limestone to 89.6, which is in better agreement with Trofimov's value of 90.0. Trofimov's results are of particular interest in that he finds magmatic minerals to have the same average  $C^{13}$  content as meteoritic matter. This is further evidence for the identity of terrestrial and meteoritic matter.

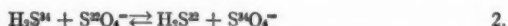
Wickman (47, 48) has published interesting results on the abundances of the carbon isotopes in plants. He investigated the  $C^{12}/C^{13}$  ratio of 150 plants representing all the major systematic groups. Characteristic differences were found to occur between the plants grown in different environments. For example, marine plants have a low  $C^{12}/C^{13}$  ratio indicating little fractionation with respect to sea water carbonates, while tropical rain forest trees have a high  $C^{12}/C^{13}$  ratio indicating large isotope fractionation. Fresh water plants and other terrestrial plants have isotope ratios somewhere in between. There is little or no overlapping of values for the marine and terrestrial plants. A means is, therefore, provided for distinguishing between them. Wickman discusses these results in terms of known isotopic fractionation processes. According to Weigl (49) the assimilation rate of  $C^{14}O_2$  is about 17 per cent less than that of  $C^{12}O_2$ , which Wickman suggests corresponds to a value of about 5 per cent in the case of  $C^{13}O_2$ . Actually, there is no theoretical basis for suggesting a value lower than half of the  $C^{14}O_2$  figure of 17 per cent. (See discussion of  $C^{13}$ ,  $C^{14}$  isotope effects in this review.) In any case there is a serious discrepancy indicated since the maximum enrichment found by Wickman is about 2 per cent. This value is in closer agreement with a factor of 1.028 for the ratio of assimilation rates of  $C^{12}$  and  $C^{13}$  from a nutrient solution by algae reported by Franck & Urey (50). Wickman suggests a cyclic process to explain his results. According to him  $CO_2$  is assimilated from the local air with slightly different reaction rates for  $C^{12}O_2$  and  $C^{13}O_2$ . The  $CO_2$  is eventually returned to the air from the soil by respiration and through the metabolism of microorganisms. According to this theory the enrichment will be smallest where the soil respiration is negligible and where the "local" atmosphere for some reason does not develop. The largest isotope effects would then be observed where the cyclic process is most intense for example, a tropical rain forest. This is in accordance with the observations. Also, in the sea the cyclic process would develop in stagnant waters. Again this is in accordance with his observations. At the present time it is difficult to reconcile the large differences in assimilation rates of  $C^{12}O_2$ ,  $C^{13}O_2$ , and  $C^{14}O_2$  measured in the laboratory with the small total variation of 2 per cent in the  $C^{12}/C^{13}$  ratio in plants.

Studies of sulphur isotope abundance ratios over the past few years present an interesting story of the sulphur isotope fractionation in geological and biological processes. The subject has been reviewed recently by Rankama (51). Previous work has shown, as reported by Stewart (16), that marked variations in the abundances of the sulphur isotopes occur in samples of terrestrial origin. Variations up to 4 and 8 per cent have been found in the  $S^{33}$  and  $S^{34}$  content respectively. This would indicate a maximum spread of



16 per cent in the  $S^{34}$  content. This year Laz, Nief & Roth (52) reported isotopic ratios for 10 samples of native sulphur and three of pyrite. Their results show a 5 per cent spread in the  $S^{34}$  content in substantial agreement with previous work. In general, sulphates are enriched and sulphides depleted in the heavy isotopes of sulphur. Pyrites extend over a middle range of isotope concentrations, and sulphur of organic origin tends to be low in heavy isotopes. Meteoritic sulphur on the other hand has been found to have a constant isotopic ratio, about in the middle of the spread for terrestrial samples and close to the values obtained for sulphur of igneous origin (53, 54). Macnamara & Thode (53) have suggested that initially terrestrial sulphur was identical in isotopic content with meteoritic sulphur, and since then isotopic fractionation has occurred above and below this base level through biological and geological processes. However, a recent investigation of Macnamara *et al.* (55) shows small variations between meteoritic and igneous rock sulphur.

Tudge & Thode (56) have calculated the isotopic exchange constant for the reaction



to be 1.074 at 25°C. favouring  $S^{34}$  in the sulphate ion. This corresponds to a maximum spread of about 8 per cent in the  $S^{32}/S^{34}$  ratio reported for sulphates and sulphides. Szabo *et al.* (57) have pointed out that the isotope exchange between sulphides and sulphates according to reaction 2 could in part take place through the well-known sulphur cycle in the sea. In this process sulphates and sulphides ( $H_2S$ ) are continually being oxidized and reduced by sulphur bacteria and plant metabolism. Recently direct evidence that the sulphur isotopes are fractionated by the bacterial reduction of sulphate was reported by Thode, Kleerekoper & McElcheran (58) and by Macnamara & Thode (59). The question arises as to how long these processes have been going on and to what extent has the sulphur cycle in the sea maintained or produced isotopic equilibrium between sulphates and sulphides. Thode, Macnamara & Fleming (60) have investigated the  $S^{34}$  content of sulphides and sulphates in shales and limestones of various geological age. Their results show a remarkable correlation between isotopic ratio and geological age. Indications are that fractionation of the sulphur isotopes between sulphates and sulphides by the biological sulphur cycle in the sea began about 800 million years ago. In the most recent samples investigated the maximum spread in the  $S^{34}$  content is about 7 per cent.

It seems fairly certain from their results that the biological sulphur cycle in the sea can and does provide a mechanism for the fractionation of the sulphur isotopes according to reaction 2. Sulphides and sulphates are continuously being deposited from the sea and appear in the sedimentary rocks. At the same time rivers are returning sulphides and sulphates eroded from the rocks to the sea. Also, volcanoes are adding sulphur in its different states



of oxidation. Thode, Macnamara & Fleming (60) point out that this inflow and outflow from the exchange processes in the sea would be much like a chemical fractionation process used to separate isotopes where material is being fed in at one concentration and removed at another. The difference is, of course, that in a natural process essentially only one simple fractionation process is involved. The fact that little or no fractionation occurred in the sulphides prior to 700 to 800 million years ago suggests that living organisms, which get their free energy to support life from the oxidation of  $H_2S$  and  $S$  did not come into existence much before that time. However, Thode points out that organic matter and living organisms must certainly have been in existence when the sulphur bacteria appeared.

#### ISOTOPE EFFECTS IN CHEMICAL KINETICS

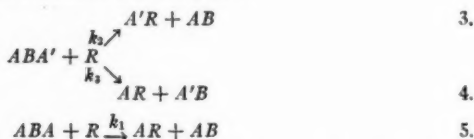
It has been known for some time that isotopes differ in their chemical properties which are related to the kinetics of reactions. In particular it was known that the isotopic atoms and molecules of hydrogen react at different rates. Since 1948 kinetic effects for the isotopes of the other light elements have received increasing attention, and during the past year a symposium was held at Notre Dame dealing largely with this subject (61). The differences in isotopic rates reported to date are of the order of 1 to 10 per cent and although small, must be taken into account in the interpretation of some tracer experiments (62). The relative rates of isotopic reactions are of particular interest in connection with rate theory. The separation factors determined give very interesting information about the reaction coordinate and provide a direct test of the transition state method of reaction kinetics. Also since the isotope factors yield the ratio of the reduced masses along the reaction coordinate they are indicative of the type of mechanism

The ratio of rate constants for reactions of isotopic molecules can, in principle, be calculated explicitly from formulas given by Eyring (63). More recently Bigeleisen (64) has developed an expression for the ratio of isotopic rate constants, which is more convenient and gives greater insight into the significant factors. The theory of isotope effects on chemical rates has been reviewed recently by Bigeleisen (65) and by Eyring & Cagle (66). Making only the assumptions inherent in the transition state hypothesis, Bigeleisen (65) obtains for the ratio of the rate constants of reactions involving isotopic molecules,

$$\frac{k^1}{k^2} = \frac{S_1 S_2^*}{S_2 S_1^*} \left( \frac{m_2^{**}}{m_1^{**}} \right)^{1/2} \left[ 1 + \sum_i \frac{3n_i - 6}{i} G(U_i) \Delta U_i - \sum_i \frac{3n_i' - 6}{i} G(U_i^*) \Delta U_i^* \right]$$

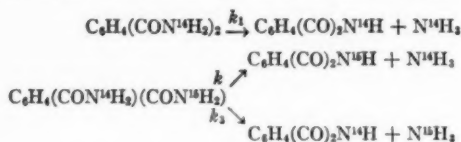
where  $S$  is the symmetry number,  $m^{**}$  is effective mass of the molecule in transition state along the reaction coordinate,  $G(U)$  is the free energy function (67) and  $\Delta U_i$  is equal to  $hc(w_1 - w_2)/kT$ . The subscripts 1 and 2 refer to the light and heavy molecules respectively. The superscript \* refers to a property of the transition state.

In general, the Bigeleisen treatment gives excellent agreement with experiment for the so-called intramolecular isotope effect. This isotope effect refers to the relative rates of reactions 3 and 4 below:



The ratio of  $k_3/k_2$  can be determined by an intercomparison of the isotopic composition of AR and AB obtained from complete reaction with the initial substrate ABA. For these rather special isotope effects where the initial state is common to both reactions the Bigeleisen expression for the separation factor reduces to the simple relation,  $k_3/k_2 = S(m_s^*/m_s^*)^{1/2}$  which is independent of temperature (68). Eyring (66) points out that the separation factor approaches  $(m^* \text{ heavy}/m^* \text{ light})^{1/2}$  at high temperatures for both intra and intermolecular isotope effects. Intramolecular isotope effects for five different reactions have been investigated to date, and the agreement between theory and experiment is excellent. However, in the more general case of the intermolecular isotope effect where we are concerned with the ratio of  $k_1/2k_2$  the theoretical treatment is more difficult and only approximate calculations can be made based on some model. The Bigeleisen model (64) proposed several years ago presumes that the only essential difference between the free energy functions of the normal and transition states arises from the vibration frequency of the bond ruptured in the transition state. The force constant in this bond is set equal to zero in the transition state, and all other frequencies are assumed to remain the same. Although this is a rough approximation, the agreement between the calculated and measured isotope effects has been fairly good for a number of reactions. For example, the Bigeleisen model yields values for the intermolecular  $C^{13}$  isotope effects in the decarboxylation of malonic acid in good agreement with experiment. Lindsay, Bourns & Thode (69) recently determined this isotope effect as a function of temperature. Their values obtained at the lower temperature are in good agreement with previously reported values and in good agreement with theory. However, their results indicate little or no temperature coefficient. This would seem to indicate that the quantum effects leading to differences in rates are small.

Stacey, Lindsay & Bourns (70) have investigated the intra and intermolecular nitrogen isotope effects in the deamination of phthalamide at 180°C. They measured the rates for the following processes:



For complete reaction the ratio  $k_2/k_3$  was 1.014 based on the  $N^{15}$  content of the evolved ammonia. This compares with a theoretical value of 1.016 calculated by Bigeleisen (71). Combining this result with those obtained for partial decomposition they obtained for  $k_1/2k_2$ ,  $k_1/2k_3$ , and  $k_1/(k_2+k_3)$  the values 0.994, 1.006, and 1.000 respectively. These intermolecular isotope effects appear to be at variance with  $C^{13}$  isotope effects found for malonic acid for which the Bigeleisen theory seems applicable. Stacey, Lindsay & Bourns have attempted to explain these results by a three center displacement reaction involving an activated complex. According to their results the lowest activation energy is found for the reaction in which a  $C^{12}-N^{14}$  bond is broken and a  $C^{12}-N^{15}$  bond is formed. Although their explanation is not complete in that it is restricted to zero point energy effects, it is clear that the Bigeleisen model for the calculation of the intermolecular isotope effect is not adequate since while the bond being ruptured in the reaction is being weakened in the transition state, there are other bonds which are appreciably strengthened.

Roe & Albenesius (72) found that in the reaction of acetone-1- $C^{14}$  with alkaline hypoiodite there is an enrichment of  $C^{14}$  in the iodoform and depletion in the acetate product. With the exception of the work of Daniels & Myerson, which recently has been reported by Daniels (73) to be in error, this is the first example of an isotope effect in which the  $C^{12}-C^{14}$  bond breaks preferentially. The authors account for this in terms of the greater stability of the carbanion I compared to carbanion II



This would seem to be analogous to the case of the phthalamide-deammoniation reaction in that while one bond is broken another bond is being strengthened in the activated complex. In the formation of the above carbanions a  $C-H$  bond is broken and a  $C-C$  bond is strengthened due to the resonance of the anion. However, the breaking of a  $C-H$  bond would be less important in regard to the carbon isotope effect than the strengthening of the  $C-C$  bond and carbanion I would be favoured. This then would result in the eventual preferential breaking of the  $C^{12}-C^{14}$  bond to form iodoform and acetate product.

Stranks & Harris (74) have studied the carbon isotope effect in the acidic decomposition of the carbonatotetramine cobaltic ion. Their results show little or no separation of the carbon isotopes. In the complex ion two of the carbonate oxygen atoms are covalently attached to the central cobaltic ion (75). The result is, therefore, not unexpected since the masses of the carbon atom will have little effect on the reduced mass across the bonds being broken.

The intermolecular isotope effect  $k_{12}/k_{14}$  in the decarboxylation at  $154^\circ C$ . of malonic-2- $C^{14}$  acid and malonic-1- $C^{14}$  has been found to be 1.07 and 1.06 respectively by Ropp & Raaen (76). In calculating the latter, the value of 1.06 reported by Roe & Hellman (77) for the intramolecular isotope effect

in malonic was used. The authors consider that the difference in the intermolecular isotope effects for the two  $C^{14}$  labelled malonic acid species is probably not significant and concluded that only a very slight increase in the effect, if a change at all, results from moving the carbon-14 label from the carboxyl to the methylene carbon. Such a shift in the label would change the zero point energy component, but not the reduced mass component of the Bigeleisen expression for the ratio of the rates of the two species.

Downes & Harris (78) have determined the isotope effect in the Cannizzaro reaction of carbon-14 labelled formaldehyde by determining the change in the specific activity of the residual reactants during the course of the reaction. The ratio of the rate constants for labelled and unlabelled formaldehyde was found to be 0.9434. It is interesting that Stevens & Atree (16) have observed that there is no fractionation of the carbon isotopes between benzoic acid and benzyl alcohol in the Cannizzaro reaction on carbon-14 labelled benzaldehyde. Brown & Holland (79) found that carbonyl- $C^{14}$  benzophenone reacts more slowly with 2,4-dinitrophenylhydrazine than does ordinary benzophenone, the rate constant ratio,  $k_{12}/k_{14}$ , being 1.099 at 27.8°.

Recently Gilman, Dunn & Hammond (80) reported that  $\phi_3Si-D$  was hydrolysed in moist piperidine to give molecular  $H_2$  almost six times as rapidly as  $\phi_3Si-H$  at room temperature. They attributed this unusual reverse effect to the displacement of a hydride ion in such a manner that a H—H bond of considerable strength, something similar to a  $H_2$  molecule, is present in the transition state. As Bigeleisen pointed out, the ratio of the partition function of HD and  $H_2$  is not large enough to explain so large an effect. Kaplan & Wiltzback (81) have investigated similar reactions, which involve the formation of  $H_2$  and have re-examined the reaction studied by Gilman, Dunn & Hammond. To enhance any isotope effects, tritium, rather than deuterium, was used in competitive measurements of  $k_T/k_H$ , the ratio of the isotopic reaction rates. For the alkaline hydrolysis of tripropyl silane-T, they obtained a  $k_T/k_H$  ratio of 0.7 and for the Gilman, Dunn, Hammond reaction a  $k_T/k_H$  ratio of  $0.796 \pm 0.004$ . This latter result does not substantiate the earlier work and is in good agreement with a theoretical value of 0.8 calculated considering only the stretching frequencies of the Si—H and H—H bonds in the proposed model (65, 66). The corresponding theoretical value of  $k_D/k_H$  is 0.9.

Becker & Beyrich (82) have investigated the effect of isotopic substitution on the collision properties of  $CO_2$ . They carried out thermal diffusion separations of isotopic species of  $CO_2$  and found that the two unsymmetrical molecules  $O^{16}C^{12}O^{17}$  and  $O^{16}C^{12}O^{18}$  of masses 45 and 46, both with symmetry number 2 (can change its rotational states by 2) behave alike, whereas the symmetrical molecule  $O^{16}C^{13}O^{16}$  of mass 45 of symmetry number 1 (can rotate in every state), behaves quite differently in a thermal diffusion column. This would seem to confirm their contention that the collision properties can change with isotopic substitution and that the isotope effect on reaction

rates may be influenced by the change in symmetry number, even for elements heavier than hydrogen.

Majury & Steacie (83) have studied the reactions of  $\text{CH}_3$  and  $\text{CD}_3$  radicals with  $\text{H}_2$  and  $\text{D}_2$  at different temperatures, the radicals being formed by the photolysis of acetone. Their results indicate no significant difference in the behaviour of the  $\text{CH}_3$  and  $\text{CD}_3$  radicals. The activation energy for the reactions of  $\text{D}_2$  was found to be  $1.6 \pm .6$  kcal. greater than that for the corresponding reaction with  $\text{H}_2$ , which is roughly in accord with theory.

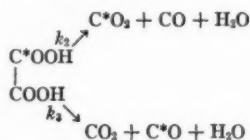
*Relative isotope effects of  $\text{C}^{13}$  and  $\text{C}^{14}$ .*—According to the theoretical treatment of relative reaction velocities of isotopic molecules, the isotope effect resulting from the substitution  $\text{C}^{14}$  for  $\text{C}^{12}$  should be nearly twice that resulting from the substitution of  $\text{C}^{13}$  for  $\text{C}^{12}$  (65, 66). However, in the decomposition of malonic acid the  $\text{C}^{14}$  isotope effects reported (84, 85) are larger than twice the  $\text{C}^{13}$  isotope effect and larger than expected on the basis of the Bigeleisen treatment. In this connection it should be pointed out that the  $\text{C}^{13}$  isotope effects are measured by means of mass spectrometers where reproducibility of 0.1 per cent is obtainable, whereas the  $\text{C}^{14}$  effects have been studied hitherto using counting techniques where reproducibility of 1 to 2 per cent is possible only the best of circumstances. The experiments of Stevens, Pepper & Lounsbury (86) are, therefore, of particular interest as they have measured  $\text{C}^{13}$  and  $\text{C}^{14}$  isotope effects in the same reaction using mass spectrometer techniques in both cases. They studied the  $\text{C}^{13}$  and  $\text{C}^{14}$  isotope effects in the decarboxylation of mesitoic acid labelled with 0.8 per cent  $\text{C}^{14}$  in the carboxyl position at  $60^\circ\text{C}$ . in 86 per cent sulphuric acid. From mass spectrometer ratios of  $\text{C}^{13}\text{O}_2/\text{C}^{12}\text{O}_2$  and  $\text{C}^{14}\text{O}_2/\text{C}^{12}\text{O}_2$  measured at the same time they obtained  $1.038 \pm 0.003$  and  $1.101 \pm .005$  for the  $k_{12}/k_{13}$  and  $k_{12}/k_{14}$  ratios respectively. The  $\text{C}^{13}$  value is in excellent agreement with that reported earlier by Bigeleisen & Bothner-By (87). The  $\text{C}^{14}$  effect on the other hand is appreciably larger than twice the  $\text{C}^{13}$  effect, a result which is at variance with theoretical treatments of isotope effects.

Yankwich, Stivers & Nystrom (88) have redetermined both the  $\text{C}^{13}$  and  $\text{C}^{14}$  intramolecular isotope effects in the decarboxylation at  $138^\circ\text{C}$ . of malonic acid labelled with  $\text{C}^{14}$  in one carboxyl group. Both the  $\text{CO}_2$  liberated directly in the reaction and that formed by oxidation over copper oxide of the acetic acid product were analysed for their  $\text{C}^{13}$  and  $\text{C}^{14}$  content, the latter by means of an ionization chamber-vibrating reed electrometer. The results, expressed as the ratio of the rate of rupture of  $\text{C}^{12}\text{—C}^{12}$  bonds to  $\text{C}^{12}\text{—C}^x$  give 1.026 and 1.103 for the  $\text{C}^{13}$  and  $\text{C}^{14}$  isotope effects respectively. The  $\text{C}^{13}$  results are in agreement with those of Bigeleisen & Friedman (89) and of Lindsay, Bourns & Thode (90) and are in fair agreement with theoretical value given by Bigeleisen (65). The  $\text{C}^{14}$  isotope effect result is in essential agreement with the work of Yankwich & Calvin (84), but is again considerably more than twice the  $\text{C}^{13}$  effect contrary to the theory. Yankwich (91) has also reported similar results for bromo malonic acid; here he finds

the  $C^{13}$  and  $C^{14}$  intramolecular isotope effects to be  $1.024 \pm .004$  and  $1.116 \pm .006$  respectively, in essential agreement with the malonic acid results.

Schmitt, Myerson & Daniels (73) have studied the  $C^{13}$  and  $C^{14}$  isotope effect in the urease catalyzed hydrolysis of urea containing approximately one atom per cent each of  $C^{13}$  and  $C^{14}$ . The relative rates of reaction of the isotope compounds were followed by the mass spectrometric analysis of the  $CO_2$ , which was evolved at successive time intervals and the following rate constant ratios were obtained:  $k^{12}/k^{13} = 1.010$  and  $k^{12}/k^{14} = 1.032$ .

Fry & Calvin (92) have measured the  $C^{13}$  and  $C^{14}$  intramolecular isotope effects in the decomposition of oxalic acid, with concentrated sulphuric acid. These effects are given as the ratio of the rate constants for the following reactions



where \* refers to either  $C^{13}$  or  $C^{14}$ . The  $C^{13}$  content of the  $CO_2$  and CO products were determined mass spectrometrically and the  $C^{14}$  contents determined with an ionization chamber vibrating reed combination. At  $80^\circ\text{C}$ . the ratio  $k_2/k_3$  was 1.0325 for oxalic acid- $C^{13}$  and 1.067 for oxalic acid- $C^{14}$ , and at  $103^\circ\text{C}$ . the ratios were 1.027 and 1.055 respectively. The  $C^{13}$  isotope effects are in satisfactory agreement with the results obtained by Lindsay, McElcheran & Thode (93). It is to be noted that the  $C^{14}$  effect is in this case very close to double the  $C^{13}$  effect at each temperature. This appears to be the only example to date in which the predicted ratio of two for the two effects has been observed.

Fry & Calvin (94) have measured the  $C^{14}$  intramolecular isotope effect in the decarboxylation of  $\alpha$ -naphthyl malonic acid-1- $C^{14}$  and phenyl malonic acid-1- $C^{14}$ , both in solution and in the liquid state near their melting points. The effects were determined by measuring the specific activities of the substituted malonic acids and the two decomposition products,  $CO_2$  and the substituted acetic acids. In the liquid decomposition of  $\alpha$ -naphthyl malonic acid and phenyl malonic acid at  $163^\circ\text{C}$ . the  $C^{14}$  isotope effect was 1.076 and 1.088 respectively. The corresponding values in solution between  $72^\circ\text{C}$ . and  $95^\circ\text{C}$ . were 1.097 and 1.13. They point out that since the  $C^{14}$  isotope effects in the malonic acid decompositions appear to be greater than twice the  $C^{13}$  effects, any model which gives satisfactory agreement with the  $C^{14}$  work will do so at the expense of disagreeing with the  $C^{13}$  work and they, therefore, conclude that until the apparent discrepancies in the experimental effects for the two isotopes have been resolved, further calculations serve little purpose.

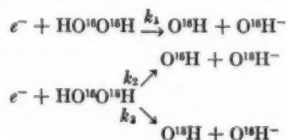
Bigeleisen (65) discusses the relative rates of  $C^{12}$ ,  $C^{13}$ , and  $C^{14}$  and concludes that for isotopes of the same element the effect on the reaction rate

should be proportional to  $\Delta M$  to a good approximation. This is not in agreement with the experiments of Stevens, Pepper & Lounsbury (86) nor those of Yankwich, Stivers & Mystrom (88). Further work needs to be done to resolve this problem.

#### ISOTOPE EFFECTS AND REACTION MECHANISMS

Three groups of workers have in the past year investigated the fractionation of the oxygen isotopes on the decomposition of  $H_2O_2$  in the presence of catalysts, oxidizing and reducing agents in order to elucidate the mechanism of the processes. This work illustrates the use of isotope fractionation factors in identifying reaction paths and in distinguishing between processes. When  $H_2O_2$  decomposes catalytically half of its oxygen is liberated as molecular oxygen and half as water, according to the reaction  $2H_2O_2 \rightleftharpoons O_2 + 2H_2O$ . In agreement with Winter & Briscoe (95) all three papers report little or no oxygen isotope exchange between  $H_2O_2$ ,  $O_2$ , and the oxygen of the catalyst or the substrate water.

Bunton & Llewellyn (96) investigated the decomposition of  $H_2O_2$  in the presence of a large number of reagents and catalysts. Details are absent, but they report small differences in the  $O^{18}$  abundance between the first and last 1 per cent of the  $O_2$  gas produced and attribute this fractionation to the easier abstraction of H atoms from  $O^{16}$  than from  $O^{18}$  since they do not consider the O—O bond to be broken in the conversion of  $H_2O_2$  to molecular oxygen. Dole *et al.* (97) studied the isotopic composition of oxygen liberated in the catalytic decomposition of  $H_2O_2$  using  $MnO_2$ ,  $Fe_2O_3$ , colloidal Au, Pt, and soluble catalase as catalysts. In each experiment the decomposition was carried to completion and the  $O^{18}$  content of the liberated  $O_2$  was compared with that of the initial  $H_2O_2$ . With the inorganic catalysts they found from 1.7 to 2.4 per cent enrichment of  $O^{18}$  in the liberated  $O_2$  gas, whereas with the enzymatic catalyst, catalase, no oxygen isotope fractionation was indicated. The latter result is in agreement with a mechanism postulated by Chance (98) for the catalytic action of catalase in the  $H_2O_2$  decomposition. According to this mechanism the O—O bond is not broken in the case of the molecular oxygen formation, and in the case of the water formation where the O—O bond is split, the group is attached to the catalyst and decomposes completely. The oxygen isotopes would not, therefore, be expected to fractionate. To explain the isotopic fractionation obtained with inorganic catalysts, Dole and his co-workers assume that the following reduction reactions are the slow steps in the process and the ones in which fractionation occurs:





From their experimental data the ratio  $k_1/2k_2$  is calculated to be 1.048 and 1.035 for the iron and manganese catalysed reactions respectively. These values compare with a theoretical value of 1.078 calculated by the method of Bigeleisen. According to the authors, the discrepancy suggests that the O—O stretching and bending frequencies in the activated complex are not entirely negligible as assumed. They also point out that if the  $\text{H}_2\text{O}_2$  or its ion  $\text{HOO}^-$  forms a tight complex with the catalyst such as  $\text{FeOOH}^{++}$  then the isotopic fractionation to be expected on splitting of the O—O bond would be reduced because of the reduction in the shift of frequencies in passing from one isotopic species to the other.

Cahill & Taube (99) investigated the isotope fractionation in the decomposition of  $\text{H}_2\text{O}_2$  in the presence of many catalysts, oxidizing and reducing agents. They discuss in detail the oxygen isotope fractionation factors involved in the decomposition of  $\text{H}_2\text{O}_2$  under various conditions. Although they find as did Dole and his co-workers that the oxygen liberated is usually enriched in  $\text{O}^{18}$  they have been able to analyse the isotope fractionation exerted by the catalysts into a fractionation factor  $f(o)$  for the production of  $\text{O}_2$ , which is characteristic of the oxidation step in the catalysis and the factor  $f(r)$  for the production of water characteristic of the reducing agent present. Their results show that little or no fractionation occurs in the oxidation step either in the presence of catalysts (where the oxidation and reduction steps go on simultaneously) or in the presence of oxidizing agents, [ $f(o) = 1$ ]. It is unlikely, therefore, that the O—O bond in  $\text{H}_2\text{O}_2$  is severed by any oxidizing agent which results in the liberation of molecular oxygen. However, in the reduction step isotopic fractionation does occur. For example, in the decomposition of  $\text{H}_2\text{O}_2$  by reducing agents such as  $\text{Fe}^{II}$ ,  $\text{Sn}^{II}$ ,  $\text{Cr}^{II}$ ,  $\text{Cu}^I$ , the fractionation factor  $f(r)$  is found to be 0.932, 0.943, 0.95, and 0.945 respectively. These large fractionation factors are explained on the basis of a two electron reduction of  $\text{H}_2\text{O}_2$  in which the O—O bond is completely severed as follows:  $\text{H}_2\text{O}_2 + 2e^- = 2\text{OH}^-$ . Little or no vibration with respect to the O—O bond will be left in the activated complex, and a maximum difference in rate between the isotopic forms of  $\text{H}_2\text{O}_2$  will be observed. From zero point energy considerations alone the difference in rates for the isotopic species  $\text{HO}^{16}\text{O}^{18}\text{H}$  and  $\text{HO}^{16}\text{O}^{16}\text{H}$  is calculated to be 6.1 per cent, which is in fair agreement with the fractionation factors [ $f(r)$ ] found for the reduction step.

Roe & Finlay (100) found no isotope effect in the pyrolysis of lithium acetate- $1\text{-C}^{14}$  to acetone and lithium carbonate. This confirms the work of Bothner-By *et al.* (101) who observed no isotope effect in the pyrolysis of barium adipate enriched in  $\text{C}^{13}$ . The lack of an isotope effect is interpreted as indicating that neither cleavage or formation of a  $\text{C}^{12}\text{—C}^{14}$  bond is involved in the step in which the symmetry of the molecule is altered. Ropp & Raaen (102) have studied the effect of varying the group R on the isotope effect  $k_{14}/k_{12}$  in the saponification of carboxyl labelled ethyl benzoates. Preliminary results indicate some variation in  $k_{14}/k_{12}$  depending on the type and position of substituent. According to the accepted mechanism for the hydrolysis reac-



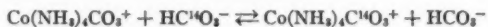
tion a transition state is formed in which the  $\pi$  linkage of the carboxyl carbon to the ring is weakened. Any substituted group such as a  $\text{OCH}_3$  in the *para* position which increases the strength of this  $\pi$  linkage would, therefore, be expected to increase the isotope effect.

Bunton & Llewellyn (103) have investigated the  $\text{C}^{13}$  isotope effects in the oxidation of oxalic acid by various reagents. It was found that the isotope effect depends on the reagent used. With the addition of  $\text{Mn}^{++}$  to the  $\text{KMnO}_4$  reagent a maximum isotope effect of 1.036 was obtained. This latter value compares with the corresponding  $\text{C}^{13}$  isotope effect reported by Lindsay, McElcheran & Thode in the dehydration of oxalic by 100 per cent sulphuric acid. They conclude that in the latter case the fission of the  $\text{C}-\text{C}$  bond is the sole rate determining step whereas with the other reagents the breaking of the  $\text{C}-\text{C}$  bond is the second stage of the reaction and only partially rate determining, the first stage being the removal of electrons from the molecule or its ions, either directly or through formation of a coordination complex.

The study of Stevens, Pepper & Lounsbury (104) on the  $\text{C}^{13}$  isotope effect in the aqueous decarboxylation of natural anthranilic acid did not show an isotope effect, unlike all other organic acid decarboxylations investigated so far. As Stevens, Pepper & Lounsbury point out,  $\text{C}-\text{C}$  bond rupture cannot be the rate determining step in this case. They have considered a number of mechanisms and suggest a proton attack on the  $\alpha$  carbon of the zwitterion as the rate determining step and most probable mechanism.

#### ISOTOPE EFFECTS IN CHEMICAL EQUILIBRIA

Separation factors for isotopic exchange reactions can be calculated provided sufficient spectroscopic data is available to calculate the partition function ratios for the isotopic molecules involved. For more complicated molecules it is usually necessary to assume some model, and the accuracy of the calculations are, of course, limited. Stranks & Harris (75) have calculated the equilibrium constant for the reaction



assuming that the two oxygen atoms of the carbonate complex are attached to the central cobaltic ion and that phosgene molecule an  $\text{XYZ}_2$  type represents a suitable model. Their calculated partition function ratios give an equilibrium constant of 0.858 which is in good agreement with their experimental value of 0.874 reported earlier. Yankwich & McNamara (105) studied a similar exchange reaction involving the complex ion  $\text{Co}(\text{en})_2\text{CO}_3^-$ . Within experimental error the equilibrium constants for the  $\text{C}^{13}$  and  $\text{C}^{14}$  exchanges were found to be unity. These results suggest a weaker binding of carbonate in the ethylene diamine complex. Taube (106) has continued his studies of the exchange of water between hydrated cation and water. He and his associates showed previously that appreciable oxygen isotope fractionation occurs through exchange equilibria of the type  $\text{A}(\text{H}_2\text{O}^{18})_n + \text{H}_2\text{O}^{18}$

$= A(H_2O^{16})_{n-1}(H_2O^{18}) + H_2O$ . The isotope effects found indicate that the heavier species is favoured in the ionic hydrates according to theoretical expectations. These isotope effects are determined by measuring the decrease in the relative activity of the heavier species which occurs with the addition of a hydrate forming cations to pure water. This is conveniently accomplished by comparing the  $O^{16}/O^{18}$  ratio of  $CO_2$  in isotopic equilibrium with the solution with that of  $CO_2$  in isotopic equilibrium with pure water. Recent results indicate that for a number of cations the isotope enrichment factor obtained increases with the molality of the solute, in a linear fashion suggesting the probable constancy of the hydration numbers of the ions up to fairly high concentrations. A trivalent ion with completely filled inner sphere  $[Co(en)_3]^{3+}$  did not show an oxygen isotope effect when added to water. This result indicates the probable identity of the hydration number and the number of water molecules in the inner sphere. Since the isotope effects measured will depend on the strength of binding in the hydrated ion, these studies provide a means for identifying the presence of hydrated ions and for determining their stability under various circumstances.

Stedman (107) has measured the equilibrium concentration of species  $NH_3$ ,  $NH_2D$ ,  $NHD_2$ , and  $ND_3$  in a sample of ammonia containing 50 atom per cent D. The analysis was carried out by an infrared absorption spectra method. The results obtained from his analysis indicate a marked deviation from the statistical distribution of deuterium and protium among the different species. It is a most surprising result and cannot be reconciled with the rule of the geometric mean, which applies approximately to other isotopic disproportionation equilibria at room temperature and above. Bigeleisen (108) has discussed this result critically. The equilibrium constant for the reaction  $2NH_3 + ND_3 = 3NH_2D$  calculated from Stedman's data is 27 (.0185) as compared to 27(1) for a random distribution of species and 27 (0.916) calculated from the partition functions of the deuterio ammonia molecules given by Kimball & Stockmayer (109). The theoretical calculations of Kimball & Stockmayer have been well confirmed by experiment in the case of deuterium exchange between  $H_2$  and  $NH_3$ . As pointed out by Bigeleisen, Stedman's results must be subject to large errors.

Eidinoff *et al.* (110) have studied the hydrogen isotope effects involved in the catalytic hydrogenation of unsaturated compounds. For the hydrogen gas-acetic acid-platinum catalyst system, they found that isotopic equilibrium in regard to  $D_2$  and  $T_2$  was established rapidly between molecular hydrogen and the carboxyl group of the acetic acid and that this equilibrium preceded the hydrogenation process. It was found that although the light hydrogen is preferentially incorporated in the compound during reduction, the pre-equilibrium between molecular hydrogen and the carboxyl group of the acetic results in an overall enrichment of deuterium and tritium in the hydrogenated compound over that of the hydrogen gas used in the reduction. The enrichment factors for the deuterium and tritium exchange between the acetic carboxyl group and molecular hydrogen were found to

be 3.83 and 6.86 respectively favouring the heavier species in the acid.

Mattraw *et al.* (111) have measured the equilibrium constant for the reaction  $H_2 + T_2 \rightleftharpoons 2HT$  mass spectrometrically. Hydrogen and tritium were found to produce the same ionization current per unit pressure within 1 per cent. They obtained for the reaction an equilibrium constant of 2.87, which compares with theoretical values of 2.56 and 2.97 at 25°C. and 127°C. respectively. These results would suggest an effective temperature in the ion source of about 100°C. which seems reasonable.

#### ISOTOPE SEPARATION

The excellent book on the theory of isotope separation by Cohen (112) was reviewed by Bigeleisen last year. Allen (113) has discussed the separation of stable isotopes by electromagnetic means, and a comparison is made with other methods, such as thermal diffusion, electrolysis, fractional distillation, and chemical exchange. Dostrovsky, *et al.* (114, 115) have discussed the operation of equipment designed for the enrichment of  $H_2O^{18}$  by the distillation of water. They apply the theory of fractional distillation to the experimental data obtained and derive the unit process separation factor  $\alpha$ .

Several papers have appeared on isotope separation processes and equipment. Bernstein (116) has discussed the enrichment of isotopes by difference in rates of irreversible isotopic reactions. The possibility was first suggested by Calvin & Yankwich (117) who patented a method for the enrichment of the carbon isotopes based on the difference in decarboxylation rates of isotopic malonic acids, also by the preferential adsorption of the lighter isotopes by living chlorophyllic organisms (118).

It is, of course, possible to multiply the small enrichment factors given by the ratio of specified rate constants for two isotopic reactions by simply carrying a reaction out to very nearly completion. The undecomposed substrate will then be enriched in the heavier isotope by an amount equivalent to several stages of separation. With an isotope separation process in mind Bernstein studied the isotope effect in the thermal decomposition of  $Ni(CO)_4$  using a flow system. The  $Ni(CO)_4$  was passed through a reaction chamber at temperatures ranging from 70–120°C. and pressure ranging from 10 to 100 mm. The undecomposed  $Ni(CO)_4$  was separated continuously. Experiments carried out at 108°C. and 117°C. run at 99.5 per cent conversion, gave overall  $C^{13}$  enrichment factors in the undecomposed  $Ni(CO)_4$  of 1.20 and 1.16 respectively. The average effect according to his analysis corresponds to a 5.3 stage process and a simple separation factor of 1.034. A possible cascade for the enrichment of isotopes by such a process is discussed.

Elder & McDonald (119) have made an exploratory investigation into the distribution of the components of a ternary isotopic mixture along a Clusius-Dickel hot wire thermal diffusion column during the approach to equilibrium. In preliminary experiments with neon, they found to exist in the column a pivot point or point of constant concentration at which the concentration of the two isotopes  $Ne^{20}$  and  $Ne^{22}$  never deviate from their

initial concentration. The distribution of the rare isotope  $\text{Ne}^{21}$  along the column at any instant was not a smooth monotonic curve as was exhibited by the other two isotopes.

#### ISOTOPE EFFECTS IN MASS SPECTRA

Since 1948 there has been considerable interest in the study of isotope effects in the dissociation of molecules by electron impact. These effects are appreciable and must be taken into account in isotope analyses with mass spectrometers. In general, isotope effects in mass spectra are thought to arise because of two effects, the application of the Franck-Condon principle to the transition from the ground state to an excited one which leads to ionization, and the relative dissociation probabilities of ions of the type  $\text{ABA}^+$  into  $\text{AB}^+$  and  $\text{A'B}^+$  where A and A' are isotopes of the same element. The experimental results to date have not been satisfactory and often two laboratories report isotope effects in opposite directions. Stein (120) has re-investigated the mass spectra of isotopic  $\text{CO}_2$  molecules and reports 0.948 and 1.022 for the ratios  $\text{C}^{13}\text{O}^+/\text{C}^{12}\text{O}^+/\text{C}^{13}\text{O}_2^+/\text{C}^{12}\text{O}_2^+$  and  $\text{C}^{13+}/\text{C}^{12+}/\text{C}^{13}\text{O}_2^+/\text{C}^{12}\text{O}_2^+$  respectively. These compare with the values 0.949 and 0.961 reported by Mohler *et al.* (121) and with the 1.007 reported by Schaeffer (122) for the latter ratio. These results indicate that mass spectrometer determinations of isotope effects in the dissociation of molecules by electron impact are subject to large errors. Newton (123) investigated the mass spectrum of both normal and  $\text{O}^{18}$  enriched  $\text{CO}_2$ . He reports a discrepancy in the ratios  $(\text{CO}^{16}\text{O}^{16})^+ / (\text{CO}^{16}\text{O}^{16})^{++}$  and  $(\text{CO}^{16}\text{O}^{18})^+ / \text{CO}^{18}\text{O}^{16++}$ . The former ratio was found to vary from 51.05 to 51.76 while the latter ratio varied from 54.93 to 56.35, the discrepancy being about 8 per cent in each case. The results indicate that  $(\text{CO}^{18}\text{O}^{18})^{++}$  has an 8 per cent lower probability of formation than  $(\text{CO}^{16}\text{O}^{16})^{++}$ . Newton suggests that this effect is due to the greater probability of fragmentation of the doubly ionized molecule containing  $\text{O}^{18}$ .

In this regard Wanless & Thode (124) have studied the mass spectra of  $\text{SO}_2$  and report an apparent preferential rupture of the heavy  $\text{S}^{34}\text{O}_2$  species to give  $\text{SO}^+$  and O. They consistently find a 1.5 per cent enrichment of  $\text{S}^{34}$  in the  $\text{SO}^+$  ions. In a similar investigation of the mass spectra of  $\text{SF}_6$  they obtained the same  $\text{S}^{32}/\text{S}^{34}$  ratio for all the ion fragments within 0.3 per cent, and the result was in agreement with the  $\text{S}^{32}/\text{S}^{34}$  ratio found for the  $\text{SO}_2^+$  ions obtained with  $\text{SO}_2$  prepared with the same sulphur. This latter agreement is not surprising since the  $\text{SO}^+$  ion currents were only a small fraction of the  $\text{SO}_2^+$  ion currents, and the  $\text{S}^{32}/\text{S}^{34}$  ratio obtained from the  $\text{SO}_2^+$  ions would not be expected to show an isotope effect. In regard to the possible preferential rupture of the heavier isotopic species, Eyring (61) has pointed out that in the dissociation of molecules by electron impact dissociation will take place rapidly, and thermodynamic equilibrium between energy levels in the molecule will not be attained. He, therefore, suggests that although the bonds of the heavier isotopic species require greater energy for rupture, there may be a greater probability of these bonds taking up that

necessary energy. However, little progress can be made in this field until the factors involved in the experimental determinations are better understood and can be controlled.

Neuert (125) has measured the difference in the ionization potentials of the protio- and deuterio-ammonia's. The ammonia's show a linear increase in ionization potential on deuterium substitution amounting to 0.22 volts between  $\text{NH}_3$  and  $\text{ND}_3$ . This compares with a difference in ionization potential of 0.18 volts found between  $\text{CH}_4$  and  $\text{CD}_4$  (126). These differences in ionization potential are large and will introduce errors in mass spectrometer analyses carried out at low electron energies. Mohler *et al.* (127) have investigated the mass spectra of deuterio acetylenes, mono deuterio benzene, and deuterio naphthalenes. For  $\text{C}_2\text{HD}$  the probability of removing the H atom is nearly twice as great as that of removing the D atom, whereas with mono deuterio benzene and naphthalene no such selectivity was found.

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# RADIOACTIVITY AND NUCLEAR THEORY<sup>1</sup>

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## INTRODUCTION

The voluminous amount of work done, both in this country and abroad, in the field of radioactivity and nuclear structure can hardly be covered completely in a review of this type. Rather than attempt an enumeration of researches, this paper will primarily be a survey of a few topics in the general field of nuclear physics. These are areas in which active research has been going on in the last few years, and which have not been covered in any detail in the previous reviews in these volumes by Libby (1), Seaborg & Templeton (2), and by Goepfert Mayer (3).

## HIGH ENERGY ACCELERATORS

One of the features of post 1946 physics research has been the construction of numerous high energy accelerators of various types. The more conventional ones, van de Graaf generators, cyclotrons, and betatrons, can even be bought from private companies. The machines that accelerate particles to above 100 Mev (betatrons, synchrocyclotrons, synchrotrons, and linear accelerators) are, of course, individually designed and built at rather great expense. Their main purpose is the investigation of nuclear forces. This is done primarily through the study of the unstable particles, mesons, which otherwise are available only in small intensities in the cosmic radiation. There are at present 11 known machines that can produce the two lightest types of mesons, the  $\pi$  meson (pion) and from it, by decay, the  $\mu$  meson (muon). These meson producing accelerators are listed in Table I.

A typical, and until recently, the most powerful machine of this type, is the University of Chicago synchrocyclotron which accelerates protons to approximately 450 Mev and produces meson beams in strong intensity with energies up to 225 Mev [Anderson *et al.* (4)].

During 1952, the Brookhaven cosmotron, the first accelerator to produce simple particles with more than one billion volts kinetic energy, started operation (5). The machine is a proton synchrotron, with particles travelling in orbits of 60 ft. diameter. They are introduced into the accelerator at 3 Mev by a van de Graaf generator once every five seconds. The acceleration is performed in small steps at one point in the orbit, with the magnetic field being gradually increased from close to zero to about 14 kilogauss as the particles gain energy. The final energy reached is about 2.3 Bev. The beam intensity is of the order of  $10^9$  particles per burst. Besides pions (and associ-

<sup>1</sup> The survey of the literature pertaining to this review was concluded in January, 1953.

TABLE I

ACCELERATORS OPERATING IN 1952 CAPABLE OF PRODUCING  $\pi$  MESONS

Type	Location	Particles Accelerated	Maximum Energy (Mev)
Synchrocyclotrons	Radiation Laboratory, Univ. of California, Berkeley, California	Protons*	345
	Rochester University, Rochester, New York	Protons*	240
	Columbia University, New York, New York	Protons*	385
	University of Chicago, Chicago, Illinois	Protons*	450
	Carnegie Inst. of Tech., Pittsburgh, Pennsylvania	Protons*	450
Betatrons	University of Illinois, Urbana, Illinois	Electrons	320
Electron synchrotrons	Radiation Laboratory, University of California, Berkeley, California	Electrons	325
	Cornell University, Ithaca, New York	Electrons	340
	Mass. Inst. of Tech., Cambridge, Massachusetts	Electrons	330
	California Inst. of Tech., Pasadena, California	Electrons	460
Proton synchrotron	Brookhaven National Laboratory, Upton, Long Island, New York	Protons	2300

\* Synchrocyclotrons usually have sufficient flexibility to accelerate other particles such as deuterons and  $\alpha$ -particles in addition to protons.

ated muons) it is expected that this machine will produce a few of the other types of mesons found in cosmic rays (3).

As regards new very high energy accelerators, an important stimulus was given to workers in the field by the theoretical investigations of Courant, Livingston & Snyder (6). They showed that combinations of magnetic lenses could be made to have a well known property of optical lenses; i.e., that divergent and convergent lenses of the same focal length could be alternated and still produce a convergent system.

With this principle in mind, the necessity no longer existed of devising magnetic fields that would guide a charged particle and keep the beam from diverging in both directions perpendicular to the trajectory. Instead, the characteristics of the magnetic field along the trajectory could be alternated

between regions in which the x component of the beam was focused and the y component defocused, and regions in which the x component was defocused and the y component was focused. With the requirement to focus in only one direction, much more efficiently focusing magnetic fields were found than were possible when both directions had to be focused simultaneously. It was shown theoretically that inclusion of these principles should not hurt, in fact should help, the efficient acceleration of particles in a synchrotron.

The use of this type of magnetic focusing is expected to reduce drastically the sizes of vacuum chambers needed in high energy machines. This would mean smaller magnets, which represent one of the largest items of cost of accelerators. For example, Courant, Livingston & Snyder outline a design for a machine to accelerate protons to 30 Bev (about ten times the maximum energy of the Brookhaven cosmotron). In this accelerator the particles would circulate in a tube of 300 foot radius, guided by 240 magnets each 8 ft. long, and constructed according to the new principle. The vacuum tube would be only 3 square in. in cross section, in contrast to the 150 square in. in the present Brookhaven machine. As a result, the amount of iron required for this machine would be about the same as for the present Brookhaven cosmotron. The new focusing principles are thus expected to reduce significantly the costs of new accelerators in the Bev range as well as provide new methods for handling beams of charged particles (protons, mesons, and electrons) produced by these accelerators.

#### STRIPPING REACTIONS AND THE INDEPENDENT PARTICLE MODEL OF THE NUCLEUS

Recent ideas concerning nuclear structure indicate that at least the most weakly bound nucleons move in independent orbits characterized by definite values of angular momentum [Libby (1), Mayer (3)]. This picture, known as the "independent particle model," has had great success in correlating observed spins of stable nuclei, observed spin changes in  $\beta$ -decay and in the decay of long lived isomers, and in explaining the fine points of nuclear binding energies and nuclear abundances. In the last two years, an additional tool for checking this model has been developed in the analysis of the angular distribution of products of "stripping" nuclear reactions involving deuterons.

The transformations induced by deuterons had already long been considered to be in a special category among nuclear reactions. Experimentally, at low deuteron energies, these reactions occur with too high a probability to be explicable by the postulate that the whole deuteron is involved. Instead, the polarization of the large, weakly bound, deuteron by the coulomb field of the target nucleus is thought to make possible the absorption of the neutron without appreciable involvement of the proton part of the deuteron.

In recent years, however, evidence had accumulated that nuclear transformations with deuterons, even at energies above the coulomb barrier, do not behave as predicted by the compound nucleus theory of nuclear reac-

tions. This theory assumes the amalgamation of the projectile with the target nucleus, and an equipartition among all the nucleons in the system of all the energy available, before the compound nucleus breaks up into the final products. The experimental results, however, indicated that  $(d,n)$  reactions with 15 to 20 Mev deuterons produce neutrons with too high an energy to be explicable on this theory, that they are concentrated in too few groups energetically, and are not only anisotropically emitted in the center of mass system, but often show maximum emission at angles different from  $0^\circ$  [Cohen & Falk (7); Falk (8); Schecter (9)]. Likewise, in the complementary  $(d,p)$  reaction, it had been established by several workers that the angular distribution of the resultant protons shows a complexity not easily explicable on the compound nucleus theory [Burrows, Gibson & Rotblat (10); Gove (11); True & Diesendruck (12); Holt & Young (13)]. All target nuclei show a nonisotropic production of protons, some with a maximum at  $0^\circ$ , others at other angles.

The situation was clarified theoretically by Butler (14, 15) who showed that an appreciable part of these reactions must proceed by a "stripping" mechanism, in which the nuclear field of the target nucleus interacts with only one of the two nucleons (either the proton or the neutron) of the large deuteron. The trajectory of the other nucleon is determined primarily by considerations of the conservation of energy and angular momentum. The main result of the latter is to produce a definite angular dependence of the path of the nonabsorbed nucleon. This angular dependence is strikingly dependent on the angular momentum of the captured particle in the target nucleus. Thus, if the particle is captured into a nuclear orbit with zero angular momentum, its partner in the deuteron proceeds with strong preference in the original direction of the deuteron; if it is captured into a nuclear orbit with unit angular momentum ( $l=1$ ), the partner proceeds preferentially in a direction about  $15^\circ$  (in a typical situation) from the original. The preferred angles increase with increasing  $l$  values. Because one of the nucleons of the original deuteron is relatively undisturbed by the nuclear encounter, the deuteron is said to be "stripped." These theoretical results were rederived and confirmed by Bhatia *et al.* (16), by Huby (17), and by Daitch & French (18). It was shown that similar considerations apply to both  $(d,p)$  and  $(d,n)$  reactions and also to  $(T,d)$   $(d,T)$  and  $(d,He^3)$  reactions [Butler & Salpeter (19); Newns (20)].

The stripping theory predicts very well the experimentally observed angular distribution of particles emitted in the forward direction (less than  $\sim 50^\circ$ ) in reactions where the product nucleus is left in a definite state of excitation. For example, the angular distribution of protons in the  $Be^9(d,p)Be^{10}$  reaction leading to the ground state of  $Be^{10}$  at four different deuteron energies between 1.1 and 14 Mev is all consistent with the stripping theory involving the capture of a neutron into a nuclear orbit with  $l=1$  [Fulbright *et al.* (21); Black (22); El-Bedewi (23)]. The complementary

$\text{Be}^9(d,n)\text{B}^{10}$  reaction has also been investigated [Pruitt, Hanna & Swartz (24); Ajzenberg (25); Bromley (26)]. Here again it has been found that the neutrons are emitted according to theory if it is assumed that the proton is captured into a state with  $l=1$ . The same is true for the 3.1 Mev excited state of  $\text{B}^{10}$  [Ajzenberg (25)]. These results are consistent with the known properties of these nuclides. The examples cited, moreover, illustrate the usefulness of this method in getting a kind of information about excited states of nuclei that is hard to obtain by other means.

In some cases, as pointed out by Bethe & Butler (27), the angular distribution of products from a stripping reaction provides a rather stringent test of the independent particle model of the nucleus [Butler (28)]. In these cases, the independent particle theory predicts capture into only one of the angular momentum states that are allowed by more general selection rules involving the spins of the original and final nucleus. The predictions have been checked in the case of the  $\text{Cl}^{35}(d,p)\text{Cl}^{36}$  and  $\text{P}^{31}(d,p)\text{P}^{32}$  reactions. In both of these, the general selection rules predict capture of the neutron into states of  $I_n=0$  or 2, whereas the independent particle model says that the lowest nuclear orbitals available are  $d$  orbitals and that therefore the neutron should be captured into a state with  $I_n=2$ . In both cases, the experimental angular distribution excludes more than a few per cent  $l=0$  contribution [King & Parkinson (29); Parkinson, Beach & King (30)]. These results lend strong support to the assignment of nucleons to definite orbital angular momentum states in a nucleus.

An interesting application of this method of investigating nuclear problems is in regard to the anomalous  $\beta$ -decay of  $\text{C}^{14}$  [Gerjuoy (31); Messiah (32)]. The spin of  $\text{C}^{14}$  has been measured to be 0; that of  $\text{N}^{14}$  is 1. Together with nuclear model predictions that the parity characteristics of  $\text{N}^{14}$  and  $\text{C}^{14}$  are the same, this would lead to the expectation that the  $\beta$ -decay of  $\text{C}^{14}$  would be an "allowed" transition. Instead, the half-life is much too long for its decay energy, indicating a "forbidden" transition. Since the parities of  $\text{C}^{14}$  and  $\text{N}^{14}$  had not actually been investigated, there was the possibility that theory and experiment could be reconciled if they were different.

Bromley and co-workers (26, 33) analyzed the angular distribution of protons and neutrons from the  $\text{C}^{13}(d,p)\text{C}^{14}$  and  $\text{C}^{13}(d,n)\text{N}^{14}$  reactions and showed that they were the same. The distribution implied, according to the Butler stripping theory, the capture of a particle in both cases into a state of unit orbital angular momentum. This means that the parity of  $\text{C}^{14}$  and  $\text{N}^{14}$  are the same, and opposite to that of  $\text{C}^{13}$ .  $\text{C}^{13}$  had already been shown by the same methods to be formed from  $\text{C}^{12}$  by the capture of a neutron into a state also with  $l=1$  [Black (22); Bromley & Goldman (33)]. These results are consistent with nuclear theory prediction that  $p$  states are being filled in this region of the nuclide chart.

Thus, the experiments indicate that the parities of  $\text{N}^{14}$  and  $\text{C}^{14}$  are the same and that they are the same as that of  $\text{C}^{13}$ , which is probably even.

The  $C^{14}$   $\beta$ -decay continues to remain one of the few that are not understood on modern  $\beta$ -ray theory.

#### ELECTRON-NEUTRON INTERACTION

The interaction between the fundamental particles, electron and neutron, has been the subject of both experimental and theoretical investigations during the last years. Experimentally the problem has been attacked in three different ways. In one, originally developed by Fermi & Marshall (34) and refined by Hammermesh, Ringo & Wattenberg (35), the anisotropy of scattering of low energy neutrons by a monatomic gas such as xenon or krypton is measured. Such an anisotropy in the scattering of particles having wavelengths of atomic dimensions can arise primarily if there is an electron-neutron force. The choice of a noble gas removes the possibility of an interaction arising from a permanent atomic magnetic moment acting on the magnetic moment of the neutron.

In the second method, developed by Rabi and co-workers (36), the total cross section of liquid bismuth for low energy neutrons was measured as a function of neutron wave length. The wave-length dependence of other interactions, such as from the small amount of neutron capture by bismuth nuclei, and from liquid structure interference, can be calculated and subtracted. The remaining wave-length dependence is used to calculate the electron-neutron interaction.

Finally, most recently, Hughes and co-workers (37, 38) have measured this interaction by determining the critical angle for internal total reflection of a beam of neutrons at a bismuth-liquid oxygen interface. Because the nuclear scattering of bismuth and oxygen are almost equal, this critical angle is very sensitive to the electron-neutron scattering cross section.

The results of all these experimental investigations are summarized in Table II. They are expressed in terms of the depth of a square well potential of radius equal to the classical electron radius which would give rise to the effects observed. The experiments agree in demonstrating the existence of an attractive potential between the electron and neutron having a depth of about 4300 ev.

TABLE II  
MAGNITUDE OF THE ELECTRON-NEUTRON INTERACTION

Method	Potential Depth (ev)	Reference
Anisotropy of neutron scattering by a noble gas	$4100 \pm 1000$	(35)
Wave length dependence of neutron scattering by liquid Bi	$5300 \pm 1000$	(36)
Total reflection of neutrons at a Bi-O interface	$4250 \pm 400$	(38)

Theoretical calculations of the electron-neutron interaction have been summarized recently by Breit (39), by Foldy (40), and by Fried (41). One approach is to take the known magnetic moment of the neutron and calculate the electromagnetic interaction to be expected with an electric charge. Foldy (42) has shown that this gives rise to an attraction close in magnitude to that observed.

On the other hand, the situation can be examined on the basis of meson theories. Here it is assumed that the neutron is part of the time a proton and a negative  $\pi$  meson according to the equation:

$$N \rightleftharpoons P + \pi^- \quad 1.$$

[Fermi & Marshall (34)]. The contribution of the state of the neutron in which a negative meson cloud surrounds a proton should then be correlated with both the magnetic moment of the neutron and the effects on an electron. Detailed calculations based on current meson theories, if normalized to give the correct neutron magnetic moment, do give rise to an electron-neutron interaction of the right magnitude, most of which can be interpreted as the Foldy effect discussed above [Borowitz (43); Fried (41)]. Unfortunately, it is generally agreed that the mathematical techniques used in these calculations are inadequate. One indication of this is the impossibility of correlating the magnetic moment of the neutron and the electron-neutron interaction, and at the same time getting closer than a factor of eight for the magnetic moment of the proton.

#### SPONTANEOUS FISSION

It had been predicted theoretically, practically at the time of the discovery of the neutron induced nuclear fission reaction, that heavy nuclei should spontaneously break up in a similar way [e.g., Bohr & Wheeler (44)]. It was anticipated that the rate of this spontaneous fission, for nuclides then known, would be much smaller than for their decay by more conventional modes ( $\alpha$ - or  $\beta$ -emission). Indeed, soon afterwards, Flerov & Petrzhak (45) observed the spontaneous fission of ordinary uranium in an ionization chamber. The rate was some million times slower than the rate of  $\alpha$ -emission. Somewhat later, the spontaneous fission of both uranium and thorium was detected by observing the neutrons emitted [Fermi and co-workers, quoted by Segrè (46); Pose and co-workers (47, 48)], and by the observation of fission tracks in photographic plates loaded with uranium and thorium [Perfilov (49)].

The interest in spontaneous fission lies partly in the anticipation that this mode of decay might become the determining factor in the half-life of certain transuranic nuclides. It is of theoretical interest because it represents a fission reaction occurring from the ground state of a nucleus. Particle or photon induced fission occurs after excitation of the nucleus by 5 Mev. or more.

In the last year the spontaneous fission rates of 11 heavy nuclides have



been published, and upper limits set for some others [Whitehouse & Galbraith (50); Hanna *et al.* (51); Segrè (46); Seaborg (52); Ghiorso *et al.* (53)]. The partial half-lives of these range from  $2 \times 10^6$  years for  $\text{Cm}^{240}$  to  $1.4 \times 10^{18}$  years for  $\text{Th}^{232}$ . Even in the case where spontaneous fission competes most effectively, namely  $\text{Cm}^{244}$ ,  $\alpha$ -emission is still some  $10^6$  times faster [Kramish (54)].

The neutron emission accompanying the spontaneous fission of  $\text{U}^{238}$  and  $\text{Th}^{232}$  has been measured quite accurately. Within the experimental error, the number of neutrons emitted in this type of fission is the same as in the thermal neutron fission of  $\text{U}^{235}$ , namely 2.5 [Segrè (46); Littler (55); Barclay, Galbraith & Whitehouse (56)].

Since the basis of the mass asymmetry in slow neutron induced fission is not understood, it is of interest to study the mass distribution in spontaneous fission. The analysis of the energy spectrum of fragments in an ionization chamber in the spontaneous fission of natural uranium by Whitehouse & Galbraith (50) shows that asymmetrical division is still the most probable. Very nearly the same energy is liberated as in the slow neutron fission of  $\text{U}^{235}$ . Similar results, although less detailed, have been obtained by Hanna *et al.* (51) in a study of the spontaneous fission of  $\text{Cm}^{242}$ . The sensitivity of this method is not sufficient, however, to tell whether symmetrical fission is more or less probable in the spontaneous case than in the neutron induced case, or whether the width of the peaks in the mass distribution curve is changed. An interesting technique for studying such details of the yield mass curve in spontaneous fission has been reported by Mac-Namara & Thode (57). They analyzed the isotopic composition of krypton and xenon taken from very old uranium minerals. The isotopic composition and relative amounts of the two gases showed that they were of fission origin and probably arose from the spontaneous fission of  $\text{U}^{238}$  during geological times.

It is generally thought that the phenomenon of spontaneous fission is related to the Gamov theory of  $\alpha$ -decay in being governed by the rate of penetration through a potential barrier. The effect of the large mass and charge of the fission fragments relative to  $\alpha$ -particles is almost compensated by the much larger kinetic energy of the fragments. Calculations of the penetrability of the fission barrier have been made by several workers on the basis of the liquid drop model of the nucleus [Bohr & Wheeler (44); Flugge (58); Frenkel (59); Frankel & Metropolis (60)]. Frenkel (59) and Frankel & Metropolis (60) deduce that the half-life for spontaneous fission ( $T_{1/2}$ ) should be related to the height of the barrier ( $\Delta E$ ) by a relation of the type

$$T_{1/2} \approx e^{-K\Delta E}.$$

2.

These liquid drop model calculations lead to values of the logarithm of the half-life that are approximately right. They fail, however, to explain the



detailed variation of  $\Delta E$  from nucleus to nucleus as determined by photo-fission thresholds or as indicated by relative spontaneous fission rates.

Looking for empirical regularities, Whitehouse & Galbraith (61), and Seaborg (62) noticed that, for almost all even- $A$ —even- $Z$  nuclides, the logarithm of the spontaneous fission half-life was a linear function of the ratio of the square of the nuclear charge to the mass number,  $Z^2/A$ . This ratio, on liquid drop theories of fission, measures the instability of a nucleus to small deformations [Bohr & Wheeler (44)]. This empirical function appeared to determine a limiting rate for spontaneous fission in the sense that all other nuclides disintegrated at a slower rate than would be calculated from this function. Using proportionality constants for equation 2 from Frankel & Metropolis (60) together with the limiting relationship between spontaneous fission half-life and  $Z^2/A$ , Seaborg (62) calculated the barrier height ( $\Delta E$ ) for the fission of any nuclide, ( $A, Z$ ), to be

$$\Delta E = (19.0 - 0.36 Z^2/A) \text{ Mev.} \quad 3.$$

The comparison of this calculated barrier height with the energy available when the nuclide ( $A-1, Z$ ) captures a thermal neutron correlates extremely well with whether the nuclide ( $A-1, Z$ ) is fissionable with thermal neutrons. This semi-empirical approach thus relates spontaneous fission to thermal neutron induced fission, and increases the reliability of predictions as to which nuclides will undergo fission upon exposure to slow neutrons.

#### POSITRONIUM

Positrons (positively charged electrons) are emitted by many artificially radioactive nuclei as well as produced in the interaction of high energy electromagnetic rays with matter. They are usually formed with appreciable amounts of kinetic energy, but lose this energy very rapidly by ionization of the surrounding material. Their eventual fate, annihilation by combination with a common negatively charged electron with the release of  $2m_0c^2$  (about 1.0 Mev) of energy, has been qualitatively understood since the discovery of positrons. The annihilation energy is predicted theoretically and observed experimentally to appear mainly as two quanta of radiation, each with  $m_0c^2$  of energy.

Recent developments in experimental techniques have made it possible to study the annihilation of positrons in considerable detail. These developments are primarily the use of scintillation counters, which detect gamma rays with more than 10 times the efficiency previously attainable, and the development of very fast electronic circuits. It is now possible to study events separated in time by as little as  $2 \times 10^{-10}$  sec. For example, it has been determined that positrons die in condensed materials in a time of the order of  $10^{-10}$  sec [DeBenedetti & Richings (63); Bell & Graham (64)]. The two  $\gamma$ -rays are emitted in almost opposite directions, the small departure from  $180^\circ$  being consistent with annihilation of most of the positrons after being

slowed down to essentially thermal energies [DeBenedetti *et al.* (65)].

The two quantum emission is the usual method of annihilation of positrons. However, it has been predicted theoretically that in condensed media positrons might disappear in about a third of a per cent of the time by the emission of three quanta of radiation, rather than the usual two [e.g., Ore & Powell (66); Lifshitz (67)]. This three quantum annihilation has now been observed by several workers [Rich (68); Stone (69)]. As expected, the three gammas are emitted in a plane and the average energy is less than  $m_0c^2$ . The fraction of such annihilations is close to that calculated theoretically [Rich (68)].

It has also been predicted by Wheeler (70), and Pirenne (71) that the situation might be more interesting in gases. As the fast positrons are slowed down by ionization of the stopping material from their original high kinetic energy, they pass through an energy region where they may capture electrons from the gaseous atoms with which they are colliding. After being slowed down, they may end up embedded in the electronic cloud of a gaseous molecule, or as a free, neutral,  $\beta^+ - e^-$  system. Such a free combination of a positron and an electron is known as "positronium."

Quantum mechanically, the positronium system is in many respects similar to the hydrogen atom system [e.g., Ruark (72)]. Two particles are involved in both cases, and the main interaction is the coulombic attraction between the opposite electric charges. Because of the lack of a heavy nucleus, however, all the energy levels of positronium are only half as deep as in the case of the hydrogen atom. For example, the ionization potential is expected to be only 6.78 ev. This is still high enough to ensure the formation of positronium in many gases.

As regards disappearance by annihilation, there appear to be two different forms of positronium. In one form, the spins of the positron and electron are oriented in opposite directions to one another. This is the singlet form, or *para*-positronium. In the other, the spins are oriented parallel to each other. This is the triplet form, or *ortho*-positronium. The two forms have the same binding energy to within  $10^{-3}$  ev [Ferrel (73); Klein & Karplus (74)], should be formed in comparable amounts, and in the absence of paramagnetic substances, should not be interconvertible. In this respect they are similar to the *ortho-para*-hydrogen molecule system.

*Para*-positronium (total spin 0) should decay by two quantum annihilation with a mean life of  $1.25 \times 10^{-10}$  sec. [Wheeler (70); Pirenne (71)]. Such a process is, however, forbidden by selection rules for *ortho*-positronium (total spin 1). The three quantum annihilation is allowed, but has a calculated mean life of  $1.4 \times 10^{-7}$  sec. [Ore & Powell (66); see also Lifshitz (67); Ivanenko & Sokolow (75) for other calculated values for the mean life of triplet positronium]. Thus, the formation of *ortho*-positronium should be detectable by the much longer half-life with respect to annihilation, and the

occurrence of the process via three quantum rather than two quantum emission.

Both methods have been used to observe *ortho*-positronium. Shearer & Deutsch (76) were the first to observe that a measurable fraction of positrons had mean lives in the  $10^{-7}$  sec. range in diamagnetic gases. Deutsch (77) showed that this was consistent with the presence of positronium in the triplet state. The addition of 3 per cent of nitric oxide to the gases destroyed the long lived positronium by inducing singlet-triplet conversion during collisions. Oxygen had a smaller effect. The quenching effect of nitric oxide could be used, therefore, to test whether or not the long lived positrons were in a positronium system. In this way, Deutsch (78) was able to show that Freon ( $\text{CCl}_2\text{F}_2$ ) at above half an atmosphere pressure was particularly suitable for forming *ortho*-positronium. Similarly, Pond (79) showed that between 11 and 19 per cent of all the positrons stopped in gases such as hydrogen, nitrogen, argon, and helium were in the *ortho*-positronium state when they were annihilated. Using delayed coincidence techniques, Deutsch (78) measured the decay constant of *ortho*-positronium to be  $\lambda = (6.8 \pm 0.7) \times 10^6 \text{ sec.}^{-1}$  in good agreement with the calculations of Ore & Powell (66). The three quantum annihilation of positrons in condensed matter and in *ortho*-positronium represents the only experimental test of a theoretical prediction concerning a three quantum process.

In his early work Deutsch (77) had shown that some of the long lived positrons that are destroyed by nitric oxide are annihilated with the emission of  $\gamma$ -rays lower in energy than the 0.505 Mev expected from two quantum annihilation. This was consistent with the theoretically predicted three quantum decay of this system, and these lower energy quanta could be used to determine the fraction of *ortho*-positronium. Pond (79) used the fact that the quanta from *ortho*-positronium could not be emitted at  $180^\circ$  with respect to each other to analyze for this system. DeBenedetti & Siegel (80, 81) completed the identification by actually observing all three quanta in the decay of *ortho*-positronium formed when positrons were stopped in dense  $\text{SF}_6$  gas. They were also able to show that the three  $\gamma$ -rays were coplanar and were predominantly of energy  $2/3 m_e c^2$ .

The reality of positronium is considerably strengthened by actual measurement of the energy of separation of the singlet and triplet states as well as observation of some of the predicted behavior of the triplet state in a magnetic field. The energy separation arises partly from the spin-spin interaction (which is responsible for the fine structure of the hydrogen atom) and partly from exchange effects peculiar to the positronium system. It was originally calculated by Pirenne (71) and Berestetski (82), and the calculations have been repeated recently by Ferrel (73) and by Klein & Karplus (74). The separation is predicted to be  $8.4 \times 10^{-4} \text{ ev}$ .

In a magnetic field the triplet state is split into two, characterized by

$m_j=0$ , and  $m_j=\pm 1$ . The wave function of the former, moreover, now has admixed in it some of the singlet character. This leads to the prediction that the  $m_j=0$  substates of the triplet state in a magnetic field should have their lifetimes shortened by the two quantum ( $\tau=10^{-10}$  sec) decay possible for singlet positronium. This predicted quenching of *ortho*-positronium by a magnetic field has been observed by Deutsch & Dulit (83), by Pond & Dicke (84), and by Wheatley & Halliday (85). All three workers get qualitatively the expected dependence on the magnetic field strength and agree that the energy separation between the singlet and triplet states of positronium in the absence of a magnetic field is close to that predicted by theory.

In addition, Deutsch & Brown (86) have detected the transitions between the  $m_j=\pm 1$  and the  $m_j=0$  substates of *ortho*-positronium in a magnetic field of about 8900 gauss. These transitions were induced by radio-frequency radiation of  $\sim 3000$  mc. From this, they also calculate the unperturbed singlet-triplet splitting to be  $8.4 \times 10^{-4}$  ev.

Besides the formation of positronium, the "chemistry" of positrons has been investigated theoretically by several authors. Wheeler (70) predicted in 1946 that at least transiently stable systems might be formed from positrons and assorted other more conventional atomic systems. Hylleraas & Ore (87) have calculated an electron affinity for positronium of at least 0.203 ev. (The hydrogen atom has an electron affinity of 0.72 ev.) Likewise, the molecule formed between a hydrogen atom and a positronium system has been investigated theoretically by Ore (88) who expects it to be stable with respect to dissociation by at least 0.07 ev. The stability of the positronium molecule, consisting of two positrons and two electrons has also been calculated [Wheeler (70); Ore (89); Hylleraas & Ore (90)]. It appears as if this molecule is stable with respect to dissociation into two positronium systems by at least 0.11 ev. (90). Other molecular systems have been investigated by Ore (91) and Simons (92). Experimentally, the evidence for a chemistry for positronium lies primarily in the observed dependence of the formation of *ortho*-positronium on the chemical nature of the stopping gas [Deutsch (76, 77)].

#### ATOMIC SYSTEMS INVOLVING MESONS

The two most common types of mesons are the  $\pi$ -mesons and the  $\mu$ -mesons [see the summary by Goeppert Mayer (3) of the present knowledge concerning fundamental particles]. Positive and negative pions have a mass equal to 276 electron masses. The neutral pion is a little lighter, having a mass of 265 electron masses. Only charged muons are known, their mass being 210 electron masses. The spontaneous natural decay of these particles proceeds according to the equations:

$$\pi^{\pm} \rightarrow \mu^{\pm} + \nu + 34 \text{ Mev} \quad 4.$$

$$\pi^0 \rightarrow 2\gamma + 135 \text{ Mev} \quad 5.$$

$$\mu^{\pm} \rightarrow e^{\pm} + 2\nu + 107 \text{ Mev}$$

6.

The half-life at rest in free space is  $1.84 \times 10^{-8}$  sec. for the decay of the charged pions, less than  $10^{-13}$  sec. for the neutral pion, and  $1.54 \times 10^{-6}$  sec. for the muon. Although positronium-like systems involving positive mesons and electrons undoubtedly are formed under certain conditions, it is not anticipated that this will affect the nature of the decay process or the half-life of the meson involved.

On the other hand, it has long been anticipated that negative mesons (both pions and muons) would form hydrogen-atom-like systems with the nuclei of atoms. These would be formed after the mesons, which are born with very high kinetic energies, lose this kinetic energy by ionization of the surrounding material. After their velocity has been reduced to about that of the valence electrons of the stopping medium (this corresponds to a kinetic energy of some kev for the mesons) they are captured by the coulomb fields of the atomic nuclei of the stopping material.

The system of an atomic nucleus with positive charge  $Z$  and a negative meson with unit negative charge, and mass equal to some 250 electronic masses, is a hydrogen-atom-like system with energy levels some 250 times deeper than the corresponding electronic system, linear dimensions also some 250 times smaller, and radiation transition probabilities approximately 250 times greater. Other than this scaling factor, the greatest difference between the mesonic and the electronic system arises from the nonnegligible nuclear size, especially in the case of heavy nuclei. This affects appreciably the position of the energy levels in the case of these heavy nuclei. Another effect, present even in light nuclei, is to make the  $2s$  level higher than the  $2p$ , making impossible the formation of a metastable meson-nucleus system [Wheeler (93)].

Fermi, Teller & Weisskopf (94) and Fermi & Teller (95) have shown theoretically that in condensed systems negative mesons are slowed down and bound in deep Bohr-like orbitals in a time short compared with their spontaneous decay lifetimes [see also Yukawa & Okayama (96); Tomonaga & Araki (97)]. Because of the large mass of the mesons relative to that of electrons, these orbitals are inside, and not much affected by the electronic cloud of the atom.

Up until this stage, the life histories of a negative  $\pi$  and  $\mu$  meson in condensed matter are very similar. However, now the great difference in the specifically nuclear interaction of pions and muons begins to play a role.  $\pi$  mesons interact very strongly with nuclei. Once they get into the K orbit, they are absorbed by the nucleus in a time very much less than  $10^{-8}$  sec. Thus, in condensed media, even in liquid hydrogen, negative pions hardly ever decay spontaneously. In higher  $Z$  materials, moreover, where the pion density at the nucleus is appreciable in the L and even M shells, the nuclear absorption may take place before the pion reaches the lowest, K, Bohr orbit [Messiah & Marshak (98)].

In contrast with the behavior of negative pions, muons interact very feebly with nuclei. As a result, when stopped in liquids or solids, all negative  $\mu$  mesons end up in K Bohr orbits of atomic nuclei. In such orbits, the relative rate at which they interact with different nuclei is determined primarily by their wave function density at the nucleus and the number of available nucleons with which to interact. In medium weight elements the nuclear reaction probability increases as  $Z_{\text{eff}}^4$ . (The  $Z_{\text{eff}}$  takes into account the finite nuclear size.) [Wheeler (93)]. As a result, in a very low atomic number element such as lithium, the mean life of negative  $\mu$  mesons is indistinguishable from that of positive  $\mu$  mesons ( $\tau = 2.22 \times 10^{-6}$  sec.) and is that for spontaneous decay according to equation 6 above [Bell & Hincks (99); see also Conversi, Pancini & Piccioni (100); Sigurgeirsson & Yamakawa (101)]. In beryllium and carbon, however, the mean life is already noticeably shortened by nuclear interactions ( $2.05 \pm .06 \mu$  sec., and  $1.98 \pm .06 \mu$  sec., respectively) [(99); see also Morewitz & Shamos (102)]. In materials composed of elements heavier than fluorine, the lifetime of negative muons is governed primarily by the rate of nuclear interaction [Ticho (103)]. For example, the lifetime in iron is  $0.16 \mu$  sec.; in copper,  $0.12 \mu$  sec.; and in mercury, lead and bismuth, it is of the order of  $0.07 \mu$  sec. [Keuffel *et al.* (104)].

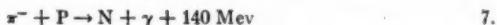
Recently this picture of the last moments of a negative meson in condensed materials has received additional support in the observation of the radiations emitted in the formation of these "mesic atoms." In the case of negative pions, the Rochester group has observed the "x-rays" corresponding to the  $2p-1s$  transition in carbon and oxygen [Camac *et al.* (105)]. The yield, per pion dying in the material, is much less than unity, indicating that even in these light elements, nuclear absorption from the  $2p$  shell and higher, is very important (98).

In the case of negative muons, workers at the Columbia cyclotron have observed the corresponding radiation in the case of aluminum (0.37 Mev), silicon (0.42 Mev), titanium (0.90 Mev), copper (1.5 Mev), and lead ( $\sim 5.3$  Mev) [Rainwater (106)]. Starting at titanium, the energies of the radiations begin to deviate more and more from those predicted on the basis of a point nucleus. For example, the predicted  $2p-1s$  transition energy on this basis for lead would be  $\sim 16$  Mev. The observed energies, agree, however, with those calculated for a negative particle with the  $\mu$ -meson mass and a homogeneously charged nucleus with a radius equal to  $1.4 \times 10^{-13} A^{1/3}$  cm. [Wheeler (93)]. As the experimental measurements are improved, this promises to be a good method of checking quantitatively nuclear radii and maybe even investigating the charge distribution inside nuclei.

#### NUCLEAR INTERACTION OF SLOW NEGATIVE PIONS

As indicated in the previous section, negative pions in condensed materials rarely decay according to equation 4, but are absorbed by the nuclei of the material. Positive pions on the other hand, because they are repelled

by nuclei, always decay after being slowed down. The nature of the nuclear interaction of slow negative pions depends strikingly on whether the nucleus is simple or complex. Panofsky *et al.* (107) have shown that when protons absorb negative pions, the two main reactions, occurring in comparable amounts, are:



Since the  $\pi^0$  decays immediately into two  $\gamma$ -rays of about 70 Mev. the main result of the interaction of negative pions with protons is the production of gamma radiation with energy greater than 50 Mev. The same workers (107) have shown that in the case of deuterium, slow negative pions react according to equations 9 or 10.



It was also shown by Panofsky and co-workers (107) that the high energy gamma rays formed in hydrogen and deuterium are not present when negative pions are absorbed in nuclei as light as lithium or carbon. In complex nuclei, therefore, it appears as if a good fraction of the rest energy of the pion is made available for excitation.

Most of the information concerning this excitation of complex nuclei has been obtained by the photographic emulsion technique [Perkins (108); Adelman & Jones (109); Cheston & Goldfarb (110); Adelman (111); Menon *et al.* (112)]. In these studies, the "stars" produced when a pion is absorbed by one of the nuclei in the emulsion are examined. Each "prong" in such a star corresponds to the emission of a charged particle.

The simplest studies involve classification of the stars according to the number of prongs. With more examination, the energy of particles, whether they are singly or doubly charged, and even whether the nucleus disrupted was a light nucleus (C, N, or O) or a heavy one (Ag or Br) in the emulsion, can be established.

The prong distribution in slow  $\pi^-$  induced stars in photographic emulsions is given in Table III. The O-prong stars often show a blob, indicating recoil of the residual nucleus. This is interpreted as arising from fast neutron emission, particularly by the light nuclei present. The neutrons are not detected by the emulsion, and are presumed also to be emitted in the other stars. About 55 per cent of the stars represented by such a survey are a result of capture of negative pions in the heavy nuclei (Ag or Br) of the emulsion [Menon *et al.* (112)]. In these latter, about 30 per cent of the prongs are alpha particles. Half of the prongs from stars originating in light nuclei (C, N, or O) are  $\alpha$ -particles.

The energy distribution of the protons in stars induced in silver and bromine has also been determined. According to Menon *et al.* (112), the distri-



bution has a maximum at about 9.5 Mev, which is reasonable in view of the coulomb barrier present in nuclei near silver and bromine. However, in about ten per cent of the stars, there are protons with energies above 30 Mev (110, 111, 112). Some of these high energy protons have as much as 85 Mev. These, of course, could not be the result of an evaporation mechanism of emission.

TABLE III  
PRONG DISTRIBUTION IN SLOW  $\pi^-$  INDUCED STARS IN  
PHOTOGRAPHIC EMULSIONS  
[Adelman (111)]

Number of Prongs	0*	1	2	3	4	5	6
Fraction of Stars	.28	.23	.23	.16	.076	.014	.001

\* O-prong stars are  $\pi^-$  endings in a photographic emulsion with no heavy charged particle seen. The fraction of such events listed in the table is taken from Menon *et al.* (112).

If charged particles are given out when negative pions are absorbed in nuclei, it is to be expected that even more neutrons would be emitted. These neutrons have recently been directly observed by Cocconi Tongiori & Edwards (113). Their experimental set-up detected primarily neutrons of energy less than 15 Mev. They found that on the average 1.6 neutrons are emitted per negative pion absorbed in carbon, 2.0 in aluminum, 6.1 in tin, and 9.3 in lead. The increasing number with increasing atomic weight is, of course, consistent with the expected lower probability of proton emission in heavy nuclei and the lower neutron binding energies.

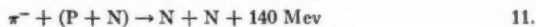
It is not surprising that the residual nuclei after the emission of particles (neutrons and charged particles) should frequently be radioactive. The pion beams at the University of Chicago synchrocyclotron are sufficiently intense to use this radioactivity for estimating the yields of products of interaction of negative pions with nuclei. For example  $C^{11}$  has been isolated from pions reacting with  $O^{16}$  and  $N^{14}$  (114). The first relatively complete study of this type has been made on the yields of radioactive nuclides formed when negative pions interact with bromine. Sugihara & Libby (115) have reported the isolation of 11 radioactive nuclides in this work. Their data indicate, for example, that in the  $(\pi^-; p, xn)$  reaction, which would correspond to a one prong star in a photographic emulsion, the maximum yield lies at  $x=4.5$ . This means that the emitted particles have carried off about 90 Mev in kinetic energy. In  $As^{75}$ , the maximum yield for the same reaction occurs at  $x=5.5$  [Turkevich & Niday (116)]; in  $I^{127}$ , the results are similar [Winsberg (117)].

The general conclusion from these studies appears to be that although a good fraction of the pion rest-mass energy is deposited in the nucleus, all



of it is not available to excite the nucleus as a whole. If it were, there would be negligible probability of concentrating 30 Mev or more in one proton, as indicated by the photographic plate studies, or of evaporating as few neutrons as are indicated by the neutron counter and radiochemical studies.

It is thought at present that these results are understandable in terms of a fundamental interaction of the negative pion with a few (2, 3, or 4) nucleons in the nucleus [Tamor (118); Fujimoto *et al.* (119); Menon *et al.* (112); Brueckner *et al.* (120); Adelman (111)]. For example, in the case of two nucleons, the initial reaction might be of the type



or



Thus the initial process would give rise to two (or more) very energetic nucleons. It is now established that such high energy particles have an appreciable probability of going through a nucleus without any collisions [Serber (121)]. The primary nucleons or the products of their first collisions inside the nucleus would then be the origin of the high energy protons seen in the photographic plate studies. Presumably, even more frequently an unseen high energy neutron escapes. For this reason the average excitation left in the nucleus would be appreciably less than 140 Mev. The number and energy distribution of protons of less than 30 Mev energy in  $\pi^-$  induced stars is said to be consistent with evaporation from a nucleus excited by at most 110 Mev [e.g., Menon *et al.* (112); Heidman & LePrince-Ringuet (122)]. The escape of a few particles carrying large amounts of kinetic energy would also explain the rather low numbers of neutrons emitted, as indicated by the neutron counter and radiochemical studies.

In the case of very heavy nuclei, it is to be expected that the absorption of a negative pion might lead to nuclear fission. This meson induced fission has now been observed in uranium in photographic plates [Al-Salam (123)] and in mercury radiochemically [Sugarman and co-workers (124)]. In both cases the process has the characteristics of very high energy induced fission [Seaborg & Templeton (2)].

#### NUCLEAR INTERACTION OF SLOW NEGATIVE $\mu$ -MESONS

After being captured in the lowest Bohr orbits of nuclei, negative muons may interact with the nucleus. As indicated in a previous section the rate of this interaction is slower than the spontaneous decay if the meson is bound to a nucleus of charge smaller than about 10; the rate of interaction is faster than the decay if the meson is bound to heavier nuclei.

The nature of this nuclear interaction has been the subject of much investigation in the last years, using both cosmic ray muons and muons resulting from the decay of accelerator produced pions. According to equation 6

above, the free decay of  $\mu$  mesons gives rise to electrons with energies in the region of 35 Mev. The rest of the 107 Mev corresponding to the rest mass of the meson is shared by the unseen neutrinos. If a nuclear interaction occurs, these decay electrons are no longer present [e.g., Conversi *et al.* (100); Perkins (125)]. However, the absorption of a muon by a nucleus does not produce the disruption to be expected from the deposition of the  $\sim 107$  Mev. in the nucleus. For example, cloud chamber studies indicate that no charged particles are emitted when negative muons stop in thin lead and aluminum plates [Chang (126); Cool *et al.* (127); Wang & Jones (128)]. Likewise, early photographic plate studies showed that when cosmic ray negative muons stop in emulsions, less than 10 per cent of the time are heavy charged particles emitted [e.g., Camerini *et al.* (129); Perkins (125)]. In support of these observations, Voorhees & Street (130) using an AgCl counter, found that the average energy associated with heavy charged particles following negative muon capture by a nucleus is probably less than 3 Mev. These results are in strong contrast with the "stars" observed in the majority of the cases when negative pions stop in matter or when fast neutrons or protons ( $\sim 90$  Mev) interact with nuclei.

Another possibility would be to have the rest energy of the muon liberated as electromagnetic radiation. At least three experiments have been performed that set low limits on the emission of  $\gamma$ -rays with energies above 20 Mev when muons are captured by nuclei [Piccioni (131); Chang (126); Sard & Althaus (132)]. On the other hand Chang (126) and Keuffel *et al.* (104) have observed moderate amounts of  $\gamma$ -rays of energy less than about 5 Mev. The lack of charged particles or very energetic gammas suggests that most of the muon rest energy is being carried off by a light, neutral particle, presumably a neutrino.

In addition to the small amount of relatively weak gamma radiation, the emission of neutrons following the capture of negative cosmic ray muons by nuclei has now been definitely established by Sard and co-workers (133 to 136) [see also Groetzinger & McClure (137)]. These studies indicate that the number of neutrons is small and varies from element to element. The highest number emitted per muon absorbed is about two, by lead; aluminum and antimony emit, on the average, about 1 and 1.5 neutrons respectively; magnesium and calcium emit at most one-fifth the number given off by lead.

Recently, moreover, a small amount of charged particle emission following negative muon capture in photographic emulsions has actually been observed and studied. George & Evans (138), Fry and co-workers (139, 140, 141), and Sherman *et al.* (142) agree that in about 5 per cent of the time when a  $\mu^-$  is captured by a silver or bromine nucleus, a charged particle is emitted. Very occasionally (less than 1 per cent of the time) more than one charged particle is given off. These charged particles are of appreciably lower average energy than in  $\pi^-$  produced stars, and very energetic protons ( $> 30$  Mev)

such as are found in  $\pi^-$  stars, have not been observed. Thus, the frequency with which different numbers of charged particles are emitted and their energy distribution are different from that observed in  $\pi^-$  induced stars.

The main features of these experimental results are made reasonable by postulating that the primary interaction of a negative muon is with only one proton of the nucleus [Rosenbluth (143); Tiomno & Wheeler (144)]. This interaction is supposed to transform it into a neutron with the simultaneous production of a weightless, uncharged particle (usually assumed to be a neutrino). The equation for this process is:



This reaction, as we will see, is more than superficially analogous to the basic process in K-capture:



The muon in its K orbit can be considered at rest. As a consequence of conservation of momentum, the capture of a muon by a free proton results in a neutron having only about 5.5 Mev of kinetic energy. In the more practical situation, a proton inside a nucleus has kinetic energy to start with, and the neutron that is formed has to be given enough energy to be left in an unoccupied state inside the nucleus. As a result, the calculations of Tiomno & Wheeler (144) based on different nuclear models, indicate that the average energy given to the neutron is about 15 Mev. This neutron kinetic energy is presumably immediately converted into nuclear excitation. Thus, about 85 per cent of the muon rest energy disappears with the neutrino.

Most nuclei have neutron and proton binding energies in the range 5 to 10 Mev. At the excitations produced by muon capture on this theory, it is to be predicted that only one or two particles could be evaporated, and, because of the coulomb barrier, these would only rarely be protons or  $\alpha$ -particles. After the emission of particles, the nucleus might still be moderately excited, and it would lose this excitation energy by emitting  $\gamma$ -rays of energy 1 to 5 Mev.

This theory, therefore, gives a reasonable qualitative explanation for the number of neutrons emitted, the relative number of protons, and the occurrence of some low energy  $\gamma$ -rays, when muons are captured by nuclei.

In addition, calculations based on this theory give roughly the correct relative rates of capture of negative muons by different elements [Wheeler (93); Kennedy (145)]. The absolute rates of capture determine the coupling constant  $G_{\mu P}$ , for the basic process (13). The most recent evaluations of the experimental data [Kennedy (145); Preston (146)] give for this constant

$$G_{\mu P} = 3.2 \times 10^{-49} \text{ erg cm}^3$$

It has been pointed out by several workers that this coupling constant is, within experimental and theoretical errors, the same as for two other quite

different fundamental processes [Lee, Rosenbluth & Yang (147); Tiomno & Wheeler (144); Preston & Duret (146)]. One is the  $\mu^-$  decay, equation 6, and the other is the basic process in ordinary  $\beta$ -decay, which may be written as equation 14. The significance of this equality is still not understood. The similarity in the three processes that has been noted in the presence, in all of them, of fermions only (particles with spin  $1/2$ ).

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# RADIATION CHEMISTRY<sup>1,2</sup>

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During the period under review reports on two important meetings concerning radiation chemistry have been published, viz., the Report of the Symposium of the American Chemical Society held at Cleveland, Ohio in 1951 and the Report of the Faraday Society Discussion held in Leeds, England, in April, 1952.

## THE PRIMARY ACT

Processes concerning the primary act have been reviewed by Spiers (1). Although nothing fundamentally new has been added to our knowledge in this field, this has emphasised again the fact that the energy lost by the fast particles is ultimately used for the excitation of discrete states, for ionisation, and for giving to the secondary electrons kinetic energies below the first excitation level of the stopping atoms or molecules; any faster secondary electrons clearly would distribute their energy further between excitation and ionisation. From the point of view of radiation chemistry there has been a certain tendency to disregard the presence of excited species, although there can be no doubt that the formation of an ion pair is always accompanied by a greater or smaller number of excited atoms or molecules, corresponding to the difference between the average energy necessary to create an ion pair and the ionisation potential of the substances under consideration.

*Spatial distribution.*—In considering the spatial distributions of ionisation and excitation it should be noted that the distribution of excited species is unlikely to differ very much from that of the ions. Furthermore, the regions of dense ionisation (excitation) exist not only at the end of the primary tracks of the electrons but also at the end of the more energetic  $\delta$ -rays. In general, ionisation and excitation are concentrated in clusters along the track of the fast electron. In fact, a large proportion of the energy loss occurs in these clusters, which are also due to low energy  $\delta$ -rays. Qualitatively, there is apparently very little difference between the different locations where ions and excited molecules are produced, although it is well known that there is a certain frequency distribution of different types of clusters, i.e., clusters containing different numbers of ions and excited molecules respectively.

An important addition to our knowledge concerning the distribution of ionisation created by the passage of  $\alpha$ -particles in liquids comes from the

<sup>1</sup> The survey of the literature pertaining to this review was concluded in December, 1952.

<sup>2</sup> The following abbreviation is used: DPPH for diphenylpicryl hydrazyl.

<sup>3</sup> I should like to thank Mr. M. Day and Mr. B. Coleby for reading the manuscript and also Dr. N. Miller for supplying some of his unpublished results.

theoretical work of Kramers (2), based on the experiments of Gerritsen (3). The latter author, who studied the ionization by  $\alpha$ -particles in liquefied gases such as nitrogen, hydrogen, helium, argon (at low temperatures), concluded that the situation in liquids in general, and in liquefied gases in particular, is rather different from that in the gaseous state. It is well known that ionisation in gases can be described, at least to a first approximation, by the theory of Jaffé (4), who assumed a cylindrical distribution of the (diffusing) ions with the track of the  $\alpha$ -particles as the axis. In liquids, on the other hand, according to Gerritsen, the ions are formed by  $\delta$ -rays in small tracks perpendicular to the path of the  $\alpha$ -particles ("feather ionisation"), the number of ion pairs in each side track depending on the initial energy of the secondary electron, and these branches may show again smaller side branches if the electrons there produced have enough energy to form one or more ion pairs themselves. The corresponding theoretical considerations of Kramers are based on a recognition of the fact that, under these conditions in liquids, recombination predominates over diffusion. Thus, while Jaffé's theory can be applied in those cases where diffusion predominates, Kramers' theory should give a better approximation where recombination predominates, because it is based on the differential equation for recombination with the influence of the diffusion as a correction term. Furthermore, Gerritsen (3) has shown that Kramers' theory must be applied to the individual tracks of the "feather ionisation" created by the secondary electrons rather than to the ions along the actual path of the  $\alpha$ -particles. Although these experiments were carried out at the relatively low temperature of the liquefied gases where diffusion is bound to be somewhat suppressed, these considerations should be of some interest also for the radiation chemistry of  $\alpha$ -particles in liquids at ordinary temperatures.

From the point of view of radiation chemistry purely physical quantities are, in general, of importance only in as much as they affect the energy necessary to create a radical pair and in connection with the chemical interactions of the excited and ionised species which lead to the formation of the primary products, such as free radicals, etc.

*Gaseous ions.*—The behaviour of gaseous ions and their reactions have been summarised by Massey (5, 6) who has treated: (a) reactions leading to positive ions; (b) reactions leading to negative ions; (c) changes in the nature of the ions; (d) detachment of electrons from negative ions; and (e) recombination of ions. Among the reactions discussed by Massey are the dissociative recombination:  $AB^+ + e \rightarrow A + B$ , and the radiative recombination:  $A^+ + B^- \rightarrow AB + h\nu$ , which will be referred to later in this review.

Charge-transfer reactions of the type:  $A^+ + B \rightarrow A + B^+$ , have been considered also by Magee (7) who has collected some recent data on ionisation potentials of interest in radiation chemistry (7, p. 556).

Magee (8) has also considered processes of the type:  $A^+ + B^- \rightarrow A + B$  where  $A^+$  and  $B^-$  represent polyatomic molecular ions, and he has arrived

at the conclusion that in these cases metathetical processes such as  $A^+ + B^- \rightarrow C + D$  are not expected to occur, i.e., the reacting ions do not change their configuration. This follows immediately from the observation that during the electron transfer the Franck-Condon principle must hold; thus ruling out any appreciable rearrangement of atoms during the time of the electron transfer.

It has been suggested by Dee & Richards (9) that the radiative recombination of ions may be of importance for the mechanism of the chemical effect of  $\alpha$ -particles in aqueous solutions. In fact, it was claimed that the oxidation of, e.g., aqueous ferrous sulphate solutions under the influence of  $\alpha$ -particles is really a photochemical process, brought about by the ultraviolet light emitted in the recombination of the ions produced by the passage of the  $\alpha$ -particles. However, according to Massey (5) radiative recombinations are hardly of any importance, and it has been pointed out (10) that these processes are even less likely to occur in solutions where the probability of light emission is further reduced. This appears also from some recent work of Miller (11) who has failed to confirm the experimental observations of Dee & Richards.

In considering the reactions leading to the formation of free radicals, etc., following immediately upon the processes of ionisation and excitation it should be borne in mind that, in general, the situation in gases is rather different from that in condensed systems. Furthermore, highly polar media, such as water, again require some special considerations. These points will be illustrated by two examples which have recently attracted renewed attention.

(a) The polymerisation of acetylene: Lind (12), who has carried out a considerable amount of experimental work on this problem, has drawn attention to the interesting fact that the ionic yield of acetylene polymerisation, under the influence of  $\alpha$ -particles, is independent of the admixture of foreign gases such as He, Ne, Ar, Kr, X, N<sub>2</sub>. It is fairly obvious that the primary ionisation of a rare gas atom of a given ionisation potential ( $I$ ) can be transferred to the acetylene molecule by charge transfer whenever the condition is fulfilled, that:  $I(\text{rare gas}) > I(\text{acetylene})$ . However, some difficulty appears to arise with regard to the formation of excited molecules which, in general, accompanies the formation of ions. Burton & Magee (13) state that on the basis of Lind's experiments one is forced to the conclusion that excited molecules are removed by some (unspecified) process without effective contribution to the polymerisation reaction. A different interpretation has been proposed recently by Weiss (14). This is based on the fact that for rare gases, in particular, the energy ( $W$ ) to create an ion pair is only slightly greater than the ionisation potential ( $I$ ), and because of the relative smallness of ( $W - I$ ) it follows immediately that excitation of discrete levels is rather improbable in the case of the rare gases.

Excited molecules could still be formed, e.g., from acetylene or in the

presence of, e.g., nitrogen; however, in the gaseous state there is always a very considerable probability that the excited molecules may lose an appreciable part of their energy by radiative processes such as:  $A^* \rightarrow A + h\nu$ , which, in general, are much more probable in the gaseous state than in condensed systems. It should be pointed out that any theory of the acetylene polymerisation, under the influence of  $\alpha$ -particles, should be able to account also for the dependence of the ionic yield on the mole fraction of the admixed gas, as found by Mund *et al.* (15).

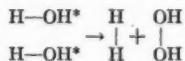
(b) Primary processes in liquid water: Dissociative recombinations have been discussed recently by Burton, Magee & Samuel (16) who have suggested that the chemical effects start from the two following classes of excited states ( $M^*$ ,  $M^\dagger$ ); the former, of comparatively small energy produced in the primary ionisation columns, whereas  $M^\dagger$  is supposed to be produced by ion neutralisation and should decompose relatively rapidly near its site of production. They have applied these considerations particularly to the radiation chemistry of water, and have given the following equations:



While it is very likely that this type of dissociative recombination may be of importance in gases and especially in the case of nonpolar liquids, a difficulty for this concept may arise in the case of polar media, such as water. In particular, the molecules of water appear to have a relatively high electron affinity as, according to the work of Bradbury & Tatel (17), condensing water vapour has a relatively large cross section for the capture of slow electrons.

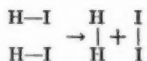
It should also be borne in mind that in the case of polar media such as water there is always a certain interaction between the electron and the ionic polarisation which it produces in its motion through the medium. In general, the electron must be pictured here as a "polaron," i.e., the electron accompanied by a cloud of phonons (i.e., excited waves of ionic polarisation). This is particularly important for very slow electrons when the kinetic energy of the electron becomes comparable with the vibrational and rotational quanta (18).

In general, in the more densely populated clusters in liquid systems there should also be a chance for mutual interaction of the primarily formed species. In particular, it might be expected that excited molecules which are formed fairly close to each other would interact. Rigg & Weiss (19) have recently arrived at the conclusion that in water, in particular, the interaction of two excited water molecules may take place according to:



and that this probably is the mechanism underlying molecular decomposition. As pictured above this reaction is similar in some respects to the well

known "molecular" decomposition of hydrogen iodide at elevated temperatures according to:



## SOLIDS

This important and interesting field offers considerable scope for the application of physical methods (e.g., paramagnetic resonance, etc.). Relatively little work leading to definite results has been reported during the period under review.

Grossweiner & Matheson (20) have reported that pure ice at low temperature was found to emit ultraviolet radiation when excited by filtered 50 kv. tungsten x-rays radiation, and self-induced luminescence has been detected in tritiated ice. Other more qualitative investigations by Stech (21) were concerned with the structural changes by the bombardment with  $\alpha$ -particles. Graphite, carbon black, anthracene, urotropine, tartaric acid, and urea were bombarded with  $\alpha$ -particles in relatively large doses, and the Debye-Scherrer diagrams of the bombarded crystals were investigated: this showed that structural changes had occurred in many cases. The transition from the amorphous to the stable crystalline modification was observed in the case of selenium. Morehead & Daniels (22) have made measurements on the energy of thermo-luminescence of lithium fluoride exposed to  $3 \times 10^4$  r of  $\gamma$ -radiation and then heated to 500°C. The bluish light emitted was found to be equivalent to 0.005 per cent of the  $\gamma$ -radiation.

Optical density measurements of crystals exposed to  $\gamma$ -radiation for long periods of time led to estimates of a value of  $10^{18}$  trapped electrons per mole. Experiments with metamict minerals have shown that the storage of energy from radioactivity, mostly from  $\alpha$ -particles, can be very much greater. The mechanism of energy storage in these minerals appears to be rather a special one and these crystals failed to exhibit their usual x-ray diffraction pattern. When the temperature was raised to 450°C., the crystal lattice was restored with the evolution of heat (about 25 cal. per gm.).

The latter observations appear to be related to the so-called "Wigner effect," i.e., the previously observed phenomenon that fast massive particles, such as  $\alpha$ -particles, protons, neutrons, and fission fragments generally possess sufficient momentum so that they can cause displacements of the atoms or ions in the lattice. Hence radiations of this type may be expected to induce atomic rearrangements even in materials normally very stable. It has been pointed out by Seitz (23) that properties of any solid are altered if appreciable fractions of its atom are displaced and if back diffusion is not sufficiently rapid to undo the influence of the displacements.

Ghormley & Levy (24) have investigated alkali halide crystals subjected to ionising radiations, ( $\text{Co}^{60}$ - $\gamma$ -rays) and have studied spectroscopically in considerable detail the F-centres and excited F-centres produced in this way.

## NONPOLAR LIQUIDS AND THEIR SOLUTIONS

The radiolysis of hydrocarbon mixtures have been investigated by Manion & Burton (25) who examined four mixtures, viz., (a) toluene-benzene; (b) cyclohexene-benzene; (c) cyclohexane-benzene; (d) cyclohexane-cyclohexene. These investigations were confined to the liquid state except for the system cyclohexane-benzene. The authors interpret their results on the basis of the formation of "energised" molecules as the primary source of hydrogen atoms, the latter giving molecular hydrogen in secondary reactions by dehydrogenation processes, such as  $\text{RH} + \text{H} \rightarrow \text{R} + \text{H}_2$ .

Radiolysis of a number of organic liquids were studied by Magat *et al.*, (26) particularly with regard to the determination of the number of free radicals formed by different ionising radiations. The methods used were (i) polymerisation initiation and (ii) reactions with the stable free radical diphenylpicrylhydrazyl (DPPH). The work was directed mainly towards (a) determination of the energy required for the formation of a free radical and (b) the action of the primary radicals. The method quoted under (ii) is based on the presumed reaction of any free radical (R) with DPPH,<sup>2</sup> leading to an addition product according to:  $\text{DPPH} + \text{R} \rightarrow (\text{DPPH} \cdot \text{R})$ . As this association product is not expected to be as deeply coloured as DPPH, which is very deeply coloured even in very dilute solutions, this reaction should be easily followed colorimetrically. As the authors point out, there are a number of limitations to this method, as it can be used only with saturated or aromatic compounds and only in the absence of water and of other compounds with reactive OH groups or possessing labile hydrogen atoms. The second method used for the "counting" of free radicals was the initiation of a polymerisation chain reaction. This is rather more ambiguous, in principle, because the mechanism of the polymerisation reaction must be fully known from a quantitative point of view, if it is to be used for this purpose. However, this work is important, as it provides the first data in this complex field, although at this stage, it is significant mainly from a qualitative point of view and as a starting point for further work.

Attempts have been made to isolate the products formed in the irradiation of DPPH particularly when dissolved in dry chloroform. Coleby (27) has reported that he was only able to isolate,  $\alpha, \alpha'$ -diphenyl- $\beta$ -picryl-hydrazine apart from unchanged DPPH; however, he got some definite indications of some other rather unstable reaction products. This appears to be confirmed by experiments reported by Wild (28) who has started a more detailed investigation of this problem. The radiolysis of pure liquid benzene and of the corresponding deuterated compound has been investigated by Gordon & Burton (29). These authors used mass spectrometric as well as ordinary chemical data for the interpretation of the mechanism of these decompositions. In the radiolysis of pure liquid  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{D}_6$  by 1.5 Mev electrons the yields of gaseous products were:

$$G(\text{H}_2) = 0.036; \quad G(\text{C}_2\text{H}_2) = 0.020 \text{ and } G(\text{D}_2) = 0.0117; \quad G(\text{C}_2\text{D}_2) = 0.0133.$$

A mechanism involving bond ruptures and rearrangements has been proposed to account for the experimental facts. The radiolysis of alkyl iodides and of alkanes has been investigated by Gevantman & Williams (30). The radiations employed were  $\text{Co}^{60}$ - $\gamma$ -rays, x-rays (45 to 50 kv.) and x-rays and electrons (2 Mev).  $\text{I}^{131}$  of a very high specific activity was used for the detection of the free radicals formed in these reactions. In the case of the alkyl iodides there are indications that the C—I bonds are broken more readily than the C—C bonds, although in the vapour state the proportion of C—C breakage is relatively higher. The radiolysis of methane suggests a primary process of the type:  $\text{CH}_4 \rightsquigarrow \text{CH}_3 + \text{H}$ , with "hot" H atoms, which react further according to:  $\text{H} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2$ . Similarly, ethane gives ethyl radicals. The primary process in the case of *n*-pentane appears to be:  $\text{C}_5\text{H}_{12} \rightsquigarrow \text{C}_3\text{H}_7 + \text{C}_2\text{H}_5 + \text{e}$ , and with *neo*-pentane:  $\text{C}(\text{CH}_3)_4 \rightsquigarrow \text{C}(\text{CH}_3)_3 + \text{CH}_3 + \text{e}$ .

Schulte *et al.* (31) have made a study of the effect of  $\gamma$ -radiation upon the decomposition of pure chloroform in an atmosphere of oxygen.

Minder & Heydrich (32) have continued their work on organic halogen compounds. A number of halogenated hydrocarbons were irradiated in solutions of alcohol or acetone. In all these cases the formation of the corresponding halogen acids was observed, and the yield of the latter was found to be proportional to the dose of the radiation and dependant also on the concentration of the solute and on the number of halogen atoms in the solute.

#### WATER AND AQUEOUS SYSTEMS

The radiation chemistry of water is still of great interest and a number of papers have been published on various aspects of this problem.

*The molecular yield ( $G_M$ ).*—In two recent papers Johnson & Allen (33) and Allen (34) have confirmed again the so-called "molecular decomposition" of water into hydrogen ( $\text{H}_2$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), in addition to the decomposition into H atoms and OH radicals, which was first postulated by Weiss (35).

With  $\gamma$ -rays or hard x-rays the yield of molecular hydrogen due to the molecular decomposition was stated to be  $G_M(\text{H}_2) = 0.6$  to 0.7 (per 100 ev).

Recent experiments by Rigg & Weiss (19) have confirmed this, and values of  $G_M(\text{H}_2) \approx 0.5$  for  $\gamma$ -rays from Ra and  $G_M(\text{H}_2) \approx 0.6$  for x-radiation (200 kv), have been obtained under a variety of conditions. Johnson & Allen (33) have carried out experiments in the presence of a number of different solutes; the determination of the molecular yield is not always quite straightforward and may be obscured by back or side reactions in the presence of certain substances in the solution. For instance, in the presence of potassium permanganate much lower values have been found by these authors, which has been confirmed by Rigg (36).

There seems little doubt that the molecular yield of the water decomposition tends to increase with increasing ionisation density of the radiation,



although an accurate comparison between very different radiations is not at present possible because of the uncertainty in the dosimetry. According to Hart (37), tritium  $\beta$ -rays give a molecular yield which is higher by about 20 per cent, as compared with  $\gamma$ -rays. Allen (34), who has reviewed the decomposition of water by natural  $\alpha$ -particles, suggests a value of  $G_M(H_2) \approx 1.9$ , although it is not certain whether this actually represents the "true" molecular yield. Allen (34) has also given a tentative picture of the process of "molecular decomposition." He starts from the familiar concept that the loss of energy by the fast electrons results in the formation of clusters and assumes that in the more densely populated clusters (containing two or more radical pairs) the energy excess over that required for the actual formation of H and OH radicals appears as heat. For this reason he called these more densely populated regions "hot-spots," and he then assumes that immediate recombination should occur in these "hot spots," according to:  $2H \rightarrow H_2$ , and  $2OH \rightarrow H_2O_2$ , although it is not clear why these reactions should be particularly favoured in these regions rather than  $H + OH \rightarrow H_2O$ .

Rigg & Weiss (19) have recently put forward a somewhat different mechanism to account for the molecular yield. This is based on the interaction of excited water molecules, the existence of which was completely neglected in earlier interpretations. Ionisation is always accompanied by excitation which follows it closely also with regard to spatial distribution. As suggested above, in the more densely populated clusters the interaction of excited water molecules according to:



could be responsible for the "molecular yield." On either of these assumptions it is to be expected that the molecular yield might increase with increasing ionisation density of the radiation, as this means also an increase of the regions of higher density of the excited molecules which would favour the interaction of the excited molecules.

*The yield of free radicals ( $G_R$ ).*—As was pointed out above there is still a fairly good case for the assumption that in water most of the radicals are formed according to:

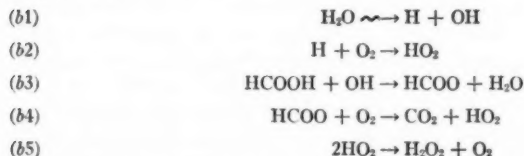


but one must take into account that there is also a considerable probability for the reaction:



as radiative deactivation is very much less probable in the condensed state. While the molecular yield ( $G_M$ ) for water can be relatively easily determined, as discussed above, the determination of the radical yield ( $G_R$ ) is much more difficult, as it must be based on the complete elucidation of the mechanism of a particular reaction on which the "counting" of the free radicals depends.

Hart (38) has determined  $G_R$  from a study of the radiation chemistry of formic acid in the presence of molecular oxygen, the mechanism of which he gives as:

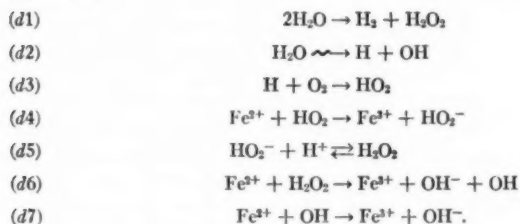


and he has obtained a value of  $G_R \approx 3.6$  radicals per 100 ev. A somewhat similar value was obtained by Hochanadel (39) from a study of the formation of hydrogen peroxide in the presence of molecular hydrogen and oxygen which he has described by the following mechanism:



Both these determinations are, however, based on the *a priori* assumption that the  $\text{HO}_2$  radicals disappear only by reaction with themselves (giving hydrogen peroxide), and we shall see later that this assumption is not justified.

It appears that a less ambiguous value for  $G_R$  can be obtained from a study of the radiation chemistry of the oxidation of ferrous ions in the presence of molecular oxygen. According to Rigg, Stein & Weiss (40) the mechanism of this reaction in dilute acid solutions of ferrous sulphate is given by:



It is of some importance to note that in this mechanism every single step has been studied and confirmed quite independently of the radiation chemistry. In fact this mechanism does not contain any novel features, and follows immediately from the Haber-Weiss mechanism (41) for the reaction between hydrogen peroxide and iron salts, which has now been fully confirmed. Taking into account the hydrogen peroxide formed by the molecular decomposition ( $G_M \approx 0.6$ ) one obtains for the radical yield in 0.8 *N* sulphuric acid a value of  $G_R \approx 4.8$  per 100 ev for  $\gamma$ -rays or hard x-rays. In principle,

this must still be considered as a lower limit because of the lack of any independent information on the extent to which the reaction  $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$  decreases the primary yield. However, the indications are that here this reverse process should play only a very minor part.

All dosimetry calculations given in this report are based on Miller's value of  $G(\text{Fe}) = 20.6$  as the experimental evidence appears to be overwhelmingly in favour of this value.

The recent work of Hardwick (42) is closely related to the question of the molecular and radical yields. This author has studied the yields in the oxidation of ferrous salts and of the reduction of ceric salts in the presence of air, by radiations of different quality and of different energies. From an examination of his own results and those of other workers he has arrived at the conclusion that the oxidation yield of ferrous salt in air-saturated solutions decreases with decreasing energy of the radiation. Thus, whereas e.g.,  $\text{Co}^{60}$ - $\gamma$ -rays and hard x-rays give yields of  $G \simeq 20$ , in the case of tritium  $\beta$ -rays the yield falls to about  $G \simeq 15.5$ . The situation is reversed in the case of the reduction of ceric salts where he finds an increase of about 70 per cent by going from  $\text{Co}^{60}$ - $\gamma$ -rays to tritium  $\beta$ -rays. Hardwick has interpreted these results in terms of Allen's "hot-spots" theory, as an increased primary recombination of H atoms and OH radicals, and in the latter reaction he assumes also the intervention of excited OH radicals. His experimental results are very interesting although they do not substantiate this theory, and the assumption of excited OH radicals seems unnecessary.

As shown above, the molecular yield (of  $\text{H}_2$  and  $\text{H}_2\text{O}_2$ ) appears to be increasing as the density of the primary ionisation increases, and this is apparently quite sufficient to explain Hardwick's results, at least on a qualitative basis: in the case of the ferrous oxidation, increase in the primary yield of molecular hydrogen should lead to a decrease in the oxidation yield, as one hydrogen atom normally contributes three oxidation equivalents in the presence of oxygen. However, the situation is not quite as clear in the case of the ceric reduction: while it is obvious that an increase in the primary yield of  $\text{H}_2\text{O}_2$  should lead to an increased amount of cerous salt produced, this is also accompanied by an increased formation of molecular hydrogen; and if this means a lower yield of hydrogen atoms then this would lead to a decrease in the yield of cerous salt, unless one takes into account the formation of H-atoms from  $\text{H}_2$  and OH radicals. Further experiments are needed here, particularly in view of the experiments of Haissinsky *et al.* (43) to clear up these points.

*The kinetics of water decomposition.*—This has been discussed particularly by Allen (34) taking into account the actual decomposition reactions and the back reactions of the products. Although we do not yet possess a complete picture of all these processes, a very promising start has been made towards the solution of this important problem.

*Formation of hydrogen peroxide.*—The formation of hydrogen peroxide has been reviewed by Bonet-Maury (44) in a very useful paper, and an

important contribution to this subject has been made by Ebert & Boag (45) who have carried out some interesting experiments on the formation and decomposition of hydrogen peroxide. Their experiments were carried out with 1 Mev. electrons and with 1.2 Mev. and 200 kv x-rays. The dose rate was varied from 300 ergs/gm. sec. to  $10^7$  ergs/gm. sec. and the total dose from  $10^6$  up to  $10^{10}$  ergs/gm. The decomposition in neutral aqueous solutions shows no dependence on the dose rate, but in acidified water the stationary hydrogen peroxide concentration, particularly at large doses, was shown to be dependent on the radiation intensity. These experiments reveal a marked difference between the 1 Mev electrons or hard x-rays on the one hand and the lower energy x-radiation on the other hand. The amount of hydrogen peroxide formed by a given radiation appears to depend on its ion density and on the pH; for a given ion density the hydrogen peroxide formation increases with increasing acidity and for a given pH the amount of hydrogen peroxide is greater for the radiation of high ion density.

Hochanadel (39) has reported new experiments on the formation of hydrogen peroxide in the presence of bromide ions. It will be recalled that such experiments have already been carried out some time ago by Fricke & Hart (46). Hochanadel (39) suggests that the increased formation of hydrogen peroxide in the presence of  $\text{Br}^-$  is due to the fact that the hydrogen peroxide, which is formed primarily by the molecular decomposition of the water, is protected from further decomposition by the radicals (H and OH) on account of the following reactions:



If this were actually the case it is to be expected that the initial yields would be quite unaffected by a change of pH of the solution. This is evidently not so as can be seen from Figure 4 in Hochanadel's paper (39) which shows that in the presence of  $\text{Br}^-$  there is a very marked increase of the initial yield of hydrogen peroxide with increasing acidity. This is clearly not accounted for by Hochanadel's equations and shows that there is something missing in his mechanism. Rigg & Weiss (19) who have also investigated this reaction, have suggested that the reason for the increased yield in acid solutions is due to the following reactions (in addition to the above):



This would lead to a very effective elimination of the hydrogen atoms, which are primarily responsible for the attack on the hydrogen peroxide.

There has again been some discussion regarding the question of the recombination of OH radicals to form hydrogen peroxide. Weiss (47) has for a long time supported the view that there is no experimental evidence for such a reaction, which is also implausible on theoretical grounds, although the chief argument against it must clearly rest on the experimental evidence.

Recently, experiments similar to those reported by Hochanadel have been carried out by Milling & Weiss (48), who have studied the hydrogen peroxide formation in the irradiation of water in the presence of molecular hydrogen and oxygen. It has been possible to elucidate the mechanism of this reaction if, in addition to the equations of Hochanadel given above, one introduces the reactions:



There are also some indications that the formation of hydrogen peroxide does not occur by reaction between two  $HO_2$  radicals but by the reaction of an  $HO_2$  radical and an  $O_2^-$  ion according to:

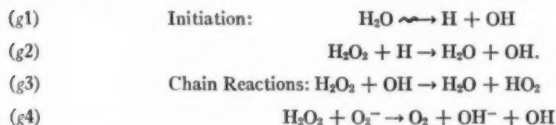


Thus, all this has again produced no evidence for the recombination of OH radicals to give hydrogen peroxide and is fully compatible with the interaction of OH radicals as suggested previously.

*Decomposition of hydrogen peroxide.*—It is of considerable interest that Hart & Matheson (49) have been able to confirm the earlier result of Fricke (50) that the yield of the  $\gamma$ -ray initiated decomposition of dilute aqueous solutions of hydrogen peroxide is proportional to the square root of the hydrogen peroxide concentration and to the inverse square root of the dose rate. They propose a chain mechanism based on the original chain reactions of Haber & Weiss (41) but assume a termolecular chain termination reaction:  $2HO_2 + H_2O_2 = 2H_2O_2 + O_2$  (rate constant:  $k_t = 2.65 \times 10^{19} l.^2 \text{ mole}^{-2} \text{ sec}^{-1}$  at  $25^\circ\text{C}.$ ) which they introduce to account for the proportionality with  $[H_2O_2]^{1/2}$ . They have also measured the propagation and termination rate constant by experiments with intermittent radiation. These experiments were carried out in paraffin coated cells at a concentration of 0.1 M hydrogen peroxide under conditions leading to a yield of about 30 molecules of oxygen per initiating radical. For the propagation step according to the reaction:  $HO_2 + H_2O_2 = H_2O + O_2 + OH$ , they give a rate constant of  $k_p = 530 l. \text{ mole}^{-1} \text{ sec}^{-1}$ .

Dainton & Rowbottom (51) raised certain objections to the termolecular chain termination as it is indeed difficult to understand that  $H_2O_2$  should be about a thousand times more effective than  $H_2O$  molecules as a third body. These authors have suggested that the yield of the hydrogen peroxide decomposition is proportional to the hydrogen peroxide concentration. However, recent experimental work of Hart & Matheson seem fairly conclusive and appears to have established the proportionality with  $[H_2O_2]^{1/2}$  in the decomposition by  $\gamma$ -rays. On the other hand, all the indications are that the photochemical decomposition is linearly dependent on the hydrogen peroxide concentration. The general relationship between the photochemical

decomposition and the decomposition of hydrogen peroxide by ionising radiations has been discussed by Weiss (52). This author has proposed the following mechanism for the radiation induced decomposition:



and he has considered a variety of possible chain breaking processes such as:



Weiss (52) advanced a different explanation for the experimentally observed rate law, based on the consideration of (a) the reaction within the "tracks" of the ionising particles, (b) the reaction between the "tracks" i.e., after overlapping (by diffusion) of the regions belonging to different "tracks" has taken place. The concept of a "track" does not refer here to any geometrical picture, which clearly could have no definite physical meaning, but refers to the totality of radicals produced by one and the same primary particle i.e., an  $\alpha$ -particle, or a primary electron in the case of  $\beta$ -rays, or a quantum of radiation in the case of x-rays or  $\gamma$ -rays. On this basis, he showed that the experimental rate law can be explained under certain assumptions which lead to the conclusion that the important part of the hydrogen peroxide decomposition occurs after the "overlapping," i.e., that the chain-breaking occurs between the radicals produced by different primary particles. Weiss' treatment is based on Jaffé's theory which has been used in an approximate, greatly simplified version but which, in this form, appears to be better adapted for the treatment of physico-chemical problems.

A number of papers have been published concerning the radiation chemistry of iron salts and particularly on the radiation induced oxidation of ferrous salts, which is also of interest from the point of view of dosimetry. Rigg, Stein & Weiss (40) have published a detailed investigation of this reaction, in the presence of oxygen as well as in deaerated solutions. The mechanism which they have proposed for the oxidation of ferrous salts in acid solutions has been discussed above in connection with the determination of  $G_R$ . If this reaction takes place at higher pH's where the  $\text{HO}_2$  radical is appreciably dissociated ( $\text{HO}_2 \rightleftharpoons \text{H}^+ + \text{O}_2^-$ ) these authors suggested that the following back reaction has to be taken into account:

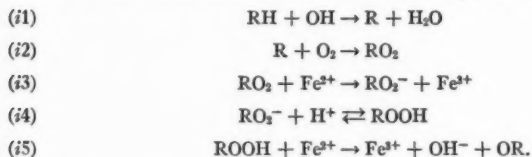


Although the reaction cannot be studied quantitatively at  $\text{pH} > 3$ , on account of the hydrolysis of the ferric salt, the mechanism represented by equations (d1) to (d7) and equation (h1) has been fully confirmed up to  $\text{pH} \sim 3$ .

In a recent paper Amphlett (53) has claimed that there is also a pH dependence of the initial yield in the ferrous oxidation, which would not be accounted for by the mechanism given above. However, Rigg & Weiss (54), who have reinvestigated this point, were not able to confirm any initial pH effect up to pH ~3. Above that, a certain pH effect could be observed which, however, is rather ambiguous because of the marked hydrolysis of the ferric salt in this region, which makes it doubtful whether the mechanism can be interpreted on the basis of a homogenous reaction. A similar difficulty seems to arise with regard to the establishment of a stationary ferrous-ferric state which, according to Amphlett (53) is reached when dilute ferrous or ferric salts are irradiated at pH = 3.1.

Dewhurst (55) has found a considerable increase in the oxidation yield in aerated solutions of ferrous sulphate in the presence of alcohols, which he has interpreted as being due to the intermediate formation of organic peroxides, which can take part in the oxidation of the ferrous salt. This is evidently a general feature of organic compounds which are capable of forming peroxides which can subsequently react with the ferrous salt, as can be seen from the work of Haissinsky *et al.* (56), who have observed a similar phenomenon with certain hydrocarbons such as xylene.

The general mechanism is evidently of the type (RH, organic "impurity").

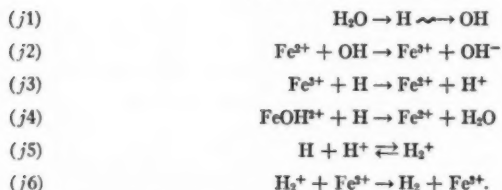


Dewhurst (55) has also made the interesting observation that the organic substance does not enter into the reactions if chloride ions are present in the solution, which thus exert a sort of protection effect, probably due to the following reactions:



Thus, under suitable conditions, in the presence of a sufficiently high concentration of  $\text{Cl}^-$ , the latter are apparently able to compete successfully for the OH radicals.

The radiation chemistry of ferrous salts in deaerated solutions has been previously investigated by Krenz & Dewhurst (57). However, their somewhat peculiar results have now been traced as being due to a contamination. This and related problems, such as the reduction of ferric salts, have been investigated by Rigg, Stein & Weiss (40) who proposed the following mechanism:



It was found that back reactions of the H atoms with  $\text{Fe}^{2+}$  as well as with the hydrolysis product  $\text{FeOH}^{2+}$  have to be taken into account. The formation and possible reactions of the hydrogen molecular ion ( $\text{H}_2^+$ ) in aqueous systems was first suggested by Weiss (58). This has now received some support from a theoretical point of view (40) and has been fully confirmed experimentally in radiation-chemical and photochemical reactions in solution (59).

A small addition to the originally proposed mechanism, as given above, has to be made if one takes into account the comparatively small amount of hydrogen peroxide formed in the molecular decomposition of the water, which should lead to a reaction corresponding to equation (d6). The ferrous oxidation was also studied in an atmosphere of hydrogen gas which leads to an inhibition of the oxidation reaction on account of the reaction:  $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ , and it has also been possible to estimate the ratio of the velocity constants of this reaction and of:  $\text{Fe}^{2+} + \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-$  (40). In the presence of fluoride or pyrophosphate ions which are known to form strong complexes with ferric ions the oxidation yield in deaerated solutions is enhanced on account of the inhibition of the back reactions (j3) and (j4), and this has also confirmed the mechanism given above (40).

Attempts were made to investigate the ferrous-ferric system not only in sulphuric acid, but also in perchloric acid solutions. However, it was found that perchlorate solutions at concentrations  $\geq 10^{-1} \text{M}[\text{ClO}_4^-]$  are quite unsuitable for this purpose. This is due to the fact that perchlorate is itself attacked by the ionising radiations leading, in general, to the formation of chlorate, except in the presence of ferrous ions, when an equivalent amount of chloride is formed (40). A more detailed investigation of the action of x-rays (200 kv.) on perchlorates in aqueous solutions by Milling, Stein & Weiss (60) has shown that this decomposition could possibly be a result of a direct effect of the radiation on the perchlorate in solution. Subsequently, somewhat similar observations have been reported by Amphlett (53). This author has also investigated the reduction of ferric salts in the presence of organic substances such as *o*-phenanthroline and dipyridyl. However, the action of these substances is evidently due not only to the fact that they can form relatively strong complexes with ferrous ions but that they can probably function also as "organic" impurities, i.e., as acceptors for the oxidising radicals.



Miller & Wilkinson (61) have studied the yield of the ferrous sulphate oxidation by  $\alpha$ -particles in 0.8 *N* sulphuric acid solutions. Assuming a value of 26.4 ev, for the energy required for the formation of an ion pair in argon by Po- $\alpha$ -particles, [which is now fairly well established (62)] the *G*-value for the ferrous oxidation in 0.8 *N* sulphuric acid, has been found to be *G*=5.9. (63). Some conclusions can be drawn also from the relative yields, e.g., these authors found a constant yield over a 24-fold range of dose rate independent, of the initial ferrous sulphate concentration when it was above  $10^{-3}M$ . Some preliminary work has been carried out on the effect of dissolved oxygen, using  $\alpha$ -particles from dissolved polonium. It was found that in 0.8 *N* sulphuric acid solution the yield of the  $\alpha$ -ray induced oxidation is reduced by a factor of 1.7 by deaeration, at initial ferrous ions concentrations from  $5 \times 10^{-4}$  to  $8 \times 10^{-3}M$ . These results, if confirmed, would be of considerable interest as they would indicate that even in the case of  $\alpha$ -particles a considerable part of the primary products consists of hydrogen atoms which are "free" to react with molecular oxygen. The mechanism of the reduction of ceric salts under different conditions has been investigated by Hardwick (64) who has found that the action of  $Co^{60}$ - $\gamma$ -rays on ceric sulphate in 0.8 *N* sulphuric acid solutions gives a yield of *G*=3.2 independent of the presence of air, which, however, is increased in the presence of molecular hydrogen to a value of *G*=6.2. Hardwick has not carried out any gas analysis, and he has confined himself to ceric sulphate solutions. Challenger & Rollefson (65) have previously reported the formation of hydrogen gas in the radiation-induced reduction of ceric salts in tritium oxide-water solutions. Ceric solutions have been investigated also in some detail by Milling, Stein & Weiss (66) with x-rays of 200 kv., in solutions of sulphuric, as well as in solutions of perchloric, acid. In both cases gas analyses have been carried out, and the reactions have been studied under different conditions. In the case of ceric perchlorate solutions the yield of the simultaneously produced chlorate was also determined. For sulphate solutions these authors were able to put forward a very simple mechanism which is represented by:



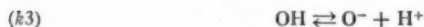
and in the presence of oxygen



They have also been able to confirm that there is an increased amount of reduction in the presence of hydrogen gas evidently due to the reaction:  $H_2 + OH \rightarrow H_2O + H$ . From this work they have concluded that in the sulphate solutions there is no reduction by OH radicals and that the yield can be fully accounted for by the primarily formed hydrogen atoms and by the hydrogen peroxide formed in the molecular decomposition of water.

In the case of ceric perchlorate solutions the situation is rather more complicated, partly as a result of the fact that the perchloric acid is also

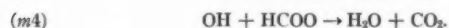
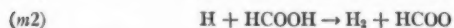
attacked, particularly if present at higher concentrations. Under the latter conditions one finds also somewhat increased yields of ceric reduction, and there is a possibility that in these solutions not only the hydrogen atoms but the OH radicals as well can act as reducing agents. It has been suggested by Haissinsky & Lefort (67) that this reduction by OH radicals goes via the formation of hydrogen peroxide. However, it is possible that the reduction is by the OH radical directly or by the anion of the OH radical,  $O^-$ , which is formed according to (68):



This would bring the reducing action of OH radicals into line with that of such substances as hydrogen peroxide or of the  $HO_2$  radical, as in both these cases the anions ( $HO_2^-$ ,  $O_2^-$  respectively) are reducing agents while the undissociated compounds are oxidizing.

The reduction of mercuric salts by x-radiation (200 kv.) has been studied by Stein, Watt & Weiss (69). As in the case of ferric salts (40) practically no reduction occurs in the presence of oxygen and only very little even in in deaerated solutions. However, in the presence of molecular hydrogen, where the stationary concentration of hydrogen atoms is much higher, appreciable reduction has been found. The pH-dependence of the yield suggests that there is a back reaction involving the hydrogen molecular ion.

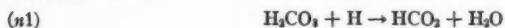
Hart (70) has studied the mechanism of the oxidation of formic acid by  $Co^{60}$ - $\gamma$ -rays and by tritium  $\beta$ -rays in deaerated aqueous solutions. He gives the following mechanism:



He has also carried out experiments with deuterated formic acid ( $D \cdot COOH$ ) in air-free solutions and on analysis finds 65 per cent HD and 35 per cent  $H_2$ ; this is an interesting result which should contribute materially to our understanding of these reactions.

The radiation chemistry of acid ferrous sulphate solutions containing dissolved carbon dioxide has been studied by Garrison & Rollefson (71) using high energy helium ions from the cyclotron as the radiation source. The principal products formed are ferric ion and hydrogen, in a proportion very close to two moles of ferric ions to one mole of hydrogen. A small fraction of the hydrogen is used to form reduction products of carbon dioxide. The most important of these is formic acid, but there are also much smaller amounts of formaldehyde and oxalate produced. The formate concentration

asymptotically approaches a definite limit which is proportional to the concentration of dissolved carbon dioxide. The proposed mechanism includes the reactions:



apart from the reactions involving ferrous ions. This mechanism seems to fit the observed data over the entire range. It is of interest that Day & Stein (72) had previously concluded from indirect evidence that  $\text{CO}_3$  in aqueous solutions can be reduced by the action of x-radiation.

The kinetics of the polymerisation of acrylonitrile in aqueous systems was studied by Collinson & Dainton (73) over a certain concentration range, using Ra- $\gamma$ -rays, 220 kv. and 50 kv. x-rays, and with dose rates ranging from  $6.6 \times 10^{12}$  to  $33,400 \times 10^{12}$  ion pairs/ml. min. At low dose rates the kinetics were consistent with a nonuniform distribution of the radicals formed from the water, whilst at high dose rates an increasing degree of uniformity was indicated. There was apparently no difference in the effects produced by the three types of radiation. The explanation given by the authors is that all three radiations give rise to radicals located in randomly distributed volume elements of water in which chemical reaction takes place, the volume elements being widely separated and independent of each other at low dose rates, but tending to overlap at high dose rates. Though this hypothesis could not be finally established the experiments appear to be in general agreement with it.

Rigg, Scholes & Weiss (74) have studied the radiation induced oxidation of ammonia in aqueous solutions in the presence of molecular oxygen. Nitrite is formed in this process, and it is concluded that this occurs apparently without any intermediate formation of hydroxylamine. The experiments indicate clearly that it is the  $\text{NH}_3$  molecule which is the reactive entity and that  $\text{NH}_4^+$ -ions are not attacked by the radicals.

Pucheault, Lefort & Haissinsky (75) have investigated the formation of hydrogen peroxide by irradiation of boric acid solutions in the French pile ZOE. The radiation was produced within the solution, e.g., through the nuclear reaction  $B(n, \alpha)$ . Haissinsky & Pucheault (76) have studied the effects of electrolytes on the formation of and decomposition of hydrogen peroxide under these conditions.

There are several other observations of interest.

Kinetic effects of various electrolytes ( $\text{LiOH}$ ,  $\text{LiClO}_4$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{MgSO}_4$ , etc.) seem to be significant. Studies on the reduction of ceric sulphate by  $\text{He}^4$  and  $\text{Li}^7$  recoils in boric acid solution are also reported. Todd and Whitcher (77) have reported briefly on the effect of oxygen in the reduction of K-iodate under the influence of x-radiation. Garrison *et al.* (78) have bombarded hydrogen saturated solutions of  $\text{C}^{14}$ -labelled formic acid with

the 40-Mev. He-ion beam of the 60-in. cyclotron. Oxalic acid, formaldehyde, and, at least eight other organic compounds were produced in this reaction. Weber & Schuler (79) have investigated the kinetics of decolorisation by x-rays (120 kv.) of dilute aqueous solutions of chlorophenolred. Graul (80) has published some experiments on the x-irradiation of aqueous solutions of methyl dichloro diethylamine (nitrogen mustard), where he observed the formation of HCl.

A review of certain topics in the formation of free radicals and atoms in water under the influence of ionising radiations was published by Dainton (81) and also by Haissinsky (82). The radiation chemistry of certain organic solutes in aqueous systems has been reviewed by Stein (83). A general discussion of radiation induced reactions in aqueous solutions has been given by Alder & Eyring (84).

#### CHEMICAL DOSIMETRY

Miller & Wilkinson (85) have devoted a considerable amount of work to the dosimetry of aqueous solutions. They have summarised their results particularly with regard to ferrous sulphate and ceric sulphate as dosimeter substances, although they have also reviewed a number of other systems. There is good agreement regarding the  $G$  value of about 20 for the radiation induced oxidation of ferrous sulphate solutions in the presence of air by  $\gamma$ -rays or hard x-rays, except for the work of Hochanadel (39) who has obtained a value of  $G = 15.5$ . Miller (86) has recently checked his value with solutions supplied by the Brookhaven and by the Chalk River laboratories and has again confirmed his earlier results. More recently he has reinvestigated the reaction over a wide range of experimental conditions; with 2 Mev x-rays he has obtained again a value of  $G = 20.3$  up to a dose rate of  $10^6$  r/min.

Thus, the majority of the experimental evidence is at present in favour of the value of  $G = 20.6$  for the ferrous sulphate oxidation in the presence of air by  $\gamma$ -rays or hard x-rays.

Some problems of dosimetry in the pile have been investigated by Wright (87). He has found that the ferrous sulphate system provides a suitable monitor for short irradiations; some of his results suggest that the chemical effect of neutrons and  $\gamma$ -radiation are not always additive in the case of a mixed source. He has also investigated for use in pile dosimetry the formation of phenolic compounds from benzene, previously studied by Stein & Weiss (88), and the decrease of optical rotation of sucrose solutions and of solid mandelic acid under the influence of ionising radiations. Chapiro (89) investigated the suitability of dilute solutions of DPPH<sup>2</sup> in chloroform for use as a chemical dosimeter. Doses of 50r or less can be detected under suitable conditions, but further work is required before this system can be accepted as a reliable dosimeter. Qualitative investigations on dosimetry were carried out by Clark *et al.* (90) who were in the first instance interested to find a sensitive colour reaction to estimate the amount of high energy radiation.

## SUBSTANCES OF BIOLOGICAL INTEREST

Allsopp & Wilson (91) have investigated the decomposition of indole by small doses of x-radiation. The initial decomposition appears to be greater in the absence, rather than in the presence, of oxygen or air. According to the authors these effects are considered to be consistent with an initial oxidation to indole-5,6-quinone, followed by oxidative condensation of this substance with unchanged indole.

Radiation effects in two-solute systems have been investigated by Dale (92), particularly with the second solute acting as a competitive acceptor of free radicals. This was demonstrated in experiments with the enzyme carboxy peptidase and with alloxazin-adenine dinucleotide. The protective power per unit mass of "protector" appears to be dependent on the concentration of the "protector."

Swallow (93) has studied the action of  $\gamma$ -radiations on aqueous solutions of cysteine. He found that dilute aqueous solutions of cysteine hydrochloride are oxidised by the action of  $\gamma$ -radiation and that for air-saturated solutions the ionic yield increases with concentration. For a 0.051 *M* solution of cysteine hydrochloride the ionic yield is 24, and this should be due to a chain reaction. In the absence of dissolved oxygen the ionic yield for a 0.051 *M* solution is 3.

Whitcher, Rotheram & Todd (94) have carried out further investigations on the action of x-rays on cysteine in aqueous solutions. Their results indicate that cysteine is formed but that there is no reduction of the cystine.

Barron & Flood (95) have studied the action of x-rays on cytochrome-*c*. Aqueous dilute solutions of ferrocytochrome-*c* are readily oxidised by x-rays, the oxidation being proportional to the dose. Catalase offers no protection and the absence of oxygen did not reduce the effect, from which the authors concluded that oxidation was brought about only by OH radicals.

Barron & Finkelstein (96) studied the effects of x-rays on some physico-chemical properties of proteins. They found that on x-irradiation of aqueous solutions of serum albumin, serum globulin, and egg albumin there was an increase in the absorption of ultraviolet light, which was most marked in the region of 2400 Å. Additions of salts greatly protected the proteins solutions against these changes. Oxygen enhanced the effect, and the authors concluded that the changes were mainly due to the oxidation of tyrosine residues and of other oxidisable groups. The viscosity of the proteins increased slightly on irradiation with 50,000 r. There were no marked changes in the electrophoretic mobility or the sedimentation constants.

Fricke (97) investigated the kinetics of thermal denaturation of egg albumin by x-rays. He showed, by the coagulation method, that x-rayed egg albumin contained different (unimolecularly denaturing) protein derivatives of decreased thermal stability. Data are given also for inhibition of the effect when the protein is irradiated together with different organic substances.

The action of x-rays on steroids in aqueous solutions has been reviewed

by Weiss (98) who has also reported some new results with cholestenone and progesterone.

*Nucleic acids and related substances in aqueous systems.*—Conway & Butler (99) have further investigated the aftereffect on the viscosity of x-irradiated deoxyribose nucleic acid solutions and maintain their previous findings that this effect occurs only in the presence of oxygen. This is a somewhat surprising result in view of the fact that oxidising radicals (OH) are present also in evacuated solutions. They have excluded the possibility that the hydrogen peroxide, which is formed during the irradiation, is responsible for the aftereffect.

A fairly detailed paper was published by Scholes & Weiss (100) who had previously found that irradiation with x-rays of nucleic acids in aqueous systems leads to some well defined chemical changes. Using doses of the order of  $10^6$  r-units, it has been observed that the fragmentation of the polynucleotides is accompanied, among other changes, by a liberation of inorganic phosphate and of small amounts of free purine bases. A deamination and some ring fission of the constituent purine and pyrimidine bases also occurs. The nature of these changes has been further investigated by a study of the behavior towards x-rays of the single purines and pyrimidines and of some of their nucleosides and nucleotides. Corresponding effects observed by the use of the hydrogen peroxide, ferrous salt (Fenton's) reagent, have confirmed that the mechanism of the action of x-rays in these dilute aqueous solutions operates via the initial splitting of the water molecules.

Similar chemical changes were also observed with much smaller doses, approaching those which are used in biological experiments. Quantitative determinations of the ammonia and free phosphate and comparison of the yields when the irradiations were performed under different experimental conditions (viz., in air, in oxygen, *in vacuo*, and in hydrogen) allow one to deduce certain features of the mechanism of attack and the nature of the reacting species involved in certain processes. In general, it has been found that the liberation of ammonia results predominantly from an attack on the amino bases by the oxidative radicals (OH and  $\text{HO}_2$ ). In the dephosphorylation process the oxidative radicals, and in certain cases also the H atoms, play an important part.

The effect of variation of pH on the yields has also been studied; these experiments show that, as in the case of the amino acids, the ionic nature of the substrate molecules is an important factor affecting their reactivity.

On the basis of these experiments, the loss of structural viscosity observed on irradiation of desoxyribonucleic solutions can be attributed to a loss of hydrogen bonding as a result of an elimination of some of the amino groups. Experiments have shown that the pyrimidines react somewhat more readily with OH radicals than the purines; this may be of some significance in the primary attack on the nucleic acid complex. Hydrolytic processes may contribute largely to the so-called "aftereffect" and these may involve further slow hydrolysis of labile phosphate esters and also of glycolic compounds,

formed by the hydroxylation of the pyrimidine ethylenic bond. Some possible mechanisms of the mode of degradation of the nucleic acids by x-rays have been discussed.

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# QUANTUM THEORY, THEORY OF MOLECULAR STRUCTURE AND VALENCE<sup>1</sup>

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The application of quantum theory to problems of molecular structure and valence continues to attract wide attention, and there is an increasing output of interesting papers. The theory has been eminently successful in providing an understanding of molecular structure and in describing the properties of molecules in a qualitative way. Perhaps its greatest success in this direction has been in its elucidation of the properties of conjugated molecules. On the other hand, progress in making calculations which are reliable quantitatively, has not been so satisfactory. For this reason increasing attention has recently been directed to the fundamental principles of the subject in order to discover where improvements of a basic kind might be made. In this review some account will be given of work of this kind, but it was considered desirable to include as well an account of some recent applications of existing approximate methods. For this reason the review falls into three main sections. There is first a discussion of current theories of molecular structure, particularly of the method of molecular orbitals. This is followed by an account of some recent applications of the method to particular problems. Finally there is a review of some of the difficulties which occur in the theory and an attempt to state in physical terms how these difficulties arise.

## CURRENT THEORIES OF MOLECULAR STRUCTURE

To appreciate the present position some preliminary account of current theories of molecular structure is desirable. The crucial problem in molecular theory is how best to solve the wave equation for many electrons in the presence of several nuclei. Even neglecting the interaction of electron spins with orbital motion and relativistic effects, the solution of the equation is still formidable. It is usual to accept the Born-Oppenheimer (1) approximation whereby the interrelation of the electronic motion and the nuclear vibrational motion is neglected, the electrons being assumed to move in the field of a fixed nuclear framework. The wave equation then takes the form (in atomic units)

$$\left\{ \sum_{j=1}^N H_j + \sum_{i>k}^N (1/r_{ik}) - E \right\} \Psi = 0, \quad (1.01)$$

where

<sup>1</sup> The survey of the literature pertaining to this review was concluded in December, 1952.

<sup>2</sup> The author gratefully acknowledges the help of Dr. G. G. Hall and Mr. P. P. Manning in the preparation of the second section of this review.

$$H_j = -\frac{1}{2}\nabla_j^2 - \sum_{\alpha} Z_{\alpha}/r_{\alpha j} \quad (1.02)$$

and  $E$  is the energy of the electrons, the total energy being

$$E + \sum_{\alpha > \beta} Z_{\alpha}Z_{\beta}/r_{\alpha\beta}. \quad (1.03)$$

$Z_{\alpha}$  is the atomic number of a typical nucleus, and  $r_{\alpha j}$  is the distance of the  $j$ th electron from it. The wave function  $\Psi$  and the energy of the electrons  $E$  will depend on the nuclear arrangement as given by the internuclear distances  $r_{\alpha\beta}$ . The great obstacle to the solution of the problem is the occurrence in the wave equation of the electrostatic potential terms  $1/r_{jk}$ . If there were no forces between the electrons, or, alternatively, if these forces could be replaced by suitable averages so that the potential of an electron could be assumed to depend only on its own space co-ordinates and not on those of any other electron, the position of molecular theory would be much more advanced than it is.

It is profitable to trace the consequences of this idealized state of affairs. Suppose that the potential of an electron is a function  $v_j$  of its space co-ordinates alone. The wave equation of the many electron system then becomes

$$\left\{ \sum_{j=1}^N H_j^* - E \right\} \Psi = 0, \quad (1.04)$$

where

$$H_j^* = -\frac{1}{2}\nabla_j^2 - v_j. \quad (1.05)$$

This equation can be solved in terms of functions which satisfy the three-coordinate equation

$$(H_j^* - \epsilon)\psi = 0. \quad (1.06)$$

It is not beyond the power of modern calculating machines to solve such an equation in three dimensional space for any disposition of nuclei. If we suppose the solutions known, say  $\psi_1, \psi_2, \dots$ , with energies  $\epsilon_1, \epsilon_2, \dots$ , then the solution of the  $N$  electron problem can be expressed in terms of products of the  $\psi$ 's, and the possible energy values consist of sums of the energies  $\epsilon_1, \epsilon_2, \dots$  of the individual orbitals. Since with each function  $\psi$  (usually called an orbital) a spin factor  $\alpha$  or  $\beta$  may be associated, the solution of the many electron problem will involve products of the type

$$\psi_1(1)\alpha(1)\psi_2(2)\beta(2) \dots, \quad (1.07)$$

and the energy will be given by

$$E = \sum_r c_r \epsilon_r, \quad (1.08)$$

where  $c_r$  is equal to 0, 1, or 2, according to the number of electrons in the orbitals of energy  $\epsilon_r$ . These solutions are exact under the conditions which have been specified.

It is at this stage that physical principles are invoked. The exclusion

principle and the principle of identity of electrons lead, as is well known, to the determinantal form of wave function for the many electron problem considered. Thus we have

$$\Psi = \det \{ \psi_1(1), \alpha(1)\psi_1(2)\beta(2), \dots \} \quad (1.09)$$

or, in some cases of degeneracy, a sum of such determinants.

*The molecular orbital theory.*—It is on the basis of this type of solution that the molecular orbital theory of valency is founded. It is assumed that the wave function of the many electron problem can be expressed in determinantal form even when the mutual fields of the electrons are included in the wave equation, but it must be realised that this type of solution can never be exact. Methods have been given for finding the best functions for orbitals  $\psi_1, \psi_2, \dots$  for this more general problem. They satisfy Hartree-Fock equations of the molecular type similar to those given by Fock for atoms (2). For the orbitals of a molecule in its normal, unexcited state these equations are

$$(H + V + A)\psi_n = \sum_m E_{mn}\psi_m \quad (1.10)$$

and are as general as can be obtained subject to the assumption that the electronic wave function can be expressed as a determinant of mutually orthogonal orbitals [Lennard-Jones (3, 4), Roothaan (5)].  $V$  is the potential field due to all the electrons, and  $A$  is a field due to all electrons of the same spin, usually called the "exchange" field. Both  $V$  and  $A$  can be defined in terms of the density matrix

$$\rho(i, j) = 2 \sum_n \psi_n(x_i)\psi_n(x_j), \quad (1.11)$$

the form valid for doubly occupied orbitals, for

$$V = \int \rho(j, j)(1/r_{ij})dx_j \quad (1.12)$$

$$A\psi_n(i) = - \int \rho(j, i)(1/r_{ij})\psi_n(x_j)dx_j. \quad (1.13)$$

The operators  $H$ ,  $V$  and  $A$  are linear, Hermitian, and have the full symmetry properties of the nuclear field. Those solutions of the above equation which satisfy the condition that  $E_{nm}$  is zero have been defined as molecular orbitals [Hall & Lennard-Jones (6)]. They are orthogonal and belong to the irreducible representations of the symmetry group.

It is important to realise that the molecular orbital theory proceeds from the case of no intercorrelation of electrons (through the  $1/r_{ij}$  terms), for which the form of wave function is exact, to the actual problem by supposing that the actual spatial correlation of the electrons can be introduced as a refinement. Thus for the hydrogen molecule in its ground state, as for the helium atom in its ground state, the wave function in the spatial co-ordinates becomes a product of the type  $\psi(1)\psi(2)$ , the antisymmetry of the total wave function being provided by the spin factors. To this

approximation there is no spatial correlation between the electrons. Each moves independently of the other except in so far as the average field is modified by the presence of the other. This is a defect of the molecular orbital theory in its simple form in that there is no spatial correlation of electrons of opposite spin, which are "paired" in the same orbital. There is, however, strong correlation of electrons with the same spin, as will be seen later. Improvements of the theory to take account of spatial correlation are given in the last main section of this review.

*The electron pair theory.*—The electron-pair or valence bond method proceeds from a different starting point. The electrostatic terms are not averaged but some are put equal to zero, as though the constituent atoms of a molecule were separated to an infinite distance. The wave function appropriate to that configuration can then be expressed as a product of the wave functions of the individual atoms, together with a series of similar products, so as to make the wave function as a whole antisymmetrical in the electrons. This wave function is then assumed to hold for finite separation of the atoms and the energy is calculated for the complete Hamiltonian, all of the electrostatic terms being included.

When there are several ways of writing the chemical structure of a molecule, these differing in the arrangement of the chemical bonds or in the assignment of electrons to correspond to ionic structures, then the method of electron pairs assigns one wave function for each such structure. The actual state of the molecule is represented by a linear sum of these basic wave functions, and the coefficients of the terms in the series are determined so as to make the calculated energy of the molecule a minimum. This superposition of possible structures, as understood in the usual chemical sense, to produce an arrangement which is more stable than any one of them is usually referred to as the "resonance" method of determining structure. It has been of great value in emphasizing the fact that the conventional method of representing a molecule by a single chemical formula is often inadequate. A chemical bond, or a series of bonds in an extended molecule, is a more complex arrangement than was formerly supposed. The simple device of representing a bond by two dots to signify the interaction of two electrons is but a crude method of picturing a complex state of affairs, as will be seen in the concluding sections of this review.

Each wave function, which represents a chemical structural form in the sense described, corresponds to such an assignment of electrons that an unpaired electron is associated with each atom participating in a "chemical bond." This unpaired electron is arranged to have the opposite spin to another electron on a combining atom. The form of the wave function then ensures that there is a strong spatial correlation of the two electrons which are said to be "paired" to form a bond. When one electron is associated with one atom, that is, has a distribution in space very near to one atom, then the other electron is automatically associated in the same sense with a second atom. This ensures that there is little probability of the two electrons being

near the same atom at the same time and so provides that one electron goes to each constituent atom on dissociation. This is an intuitive but valuable method of giving due weight to the spatial correlation of the electrons owing to the electrostatic repulsion between them. This aspect of the theory of molecular structure will be discussed in the final section of this review.

It may be said here that the molecular orbital theory and the electron pair theory are first approximations to the exact solution of molecular structure and that as each is improved by taking successively into account factors which were neglected in the simple calculations, so do both methods converge to the same general treatment.

#### SOME APPLICATIONS OF CURRENT THEORIES

*Ionization potentials of saturated molecules.*—Solutions of the molecular orbital equations, as given in equation (1.10), can be used to derive calculated values of the energy required to remove an electron from the ground state. The equations contain a set of energy parameters  $E_{nn}$ , and it has already been pointed out above that these parameters form a diagonal matrix when the solutions of the wave equations take the particular form described as molecular orbitals. Various authors have shown that the diagonal elements of this matrix ( $E_{nn}$ ) then give, to a good approximation, the energy required to remove an electron from the appropriate molecular orbitals ( $\psi_n$ ), the nuclear separation remaining fixed [Koopmans, (7), Mulliken (8, 9), Hall & Lennard-Jones (10)]. This quantity is usually called the vertical ionization potential. It may be related to observed ionization potentials, and so the calculation of the values of  $E_{nn}$  for any molecule provides a means of relating theory with experiment.

Roothaan (5) has suggested an approximate method of solving the molecular orbital equations (1.10). Each orbital is expressed as a linear combination of atomic orbitals with adjustable coefficients. These coefficients are then determined by numerical methods to make the energy a minimum and to render the system of orbitals self-consistent in the sense that the operators  $V$  and  $A$  converge to definite forms. Those solutions which reproduce themselves when  $V$  and  $A$  reach their final form then constitute the "best" solutions of the assumed type.

This self-consistent form of the molecular orbital theory has been applied with promising success to *cis*- and *trans*-butadiene by Parr & Mulliken (11) and to allene by Parr & Taylor (12). In this way Parr & Mulliken obtained an ionization potential of 9.7 ev. for butadiene, the observed value being 9.1 ev. A similar method has been used by Mulligan (13) to obtain the orbitals and energy parameters  $E_{nn}$  for carbon dioxide for a given internuclear distance. He found a value of 11.5 ev. for the lowest ionization potential as against the observed value 13.75 ev., and the next lowest as 17.9 ev. compared with the observed value of 18.0 ev.

A less direct but simpler method of obtaining these energy parameters

and hence the ionization potentials of molecules has recently been developed. Lennard-Jones (4) showed that the molecular orbital equations (1.10) could be expressed in alternative forms. Thus suppose that  $(\psi)$  represents a set of molecular orbitals, for which the energy parameters  $E_{nm}$  take a diagonal form, then other sets  $(\chi)$  can be obtained by an orthonorm transformation, and these, being normalised and orthogonal, can also be used as a basis of calculation. The operators  $H$ ,  $V$  and  $A$  in equation (1.10) remain unaltered by such a transformation. For the new set of functions the equations accordingly become

$$(H + V + A)\chi_\nu = \sum_\mu e_{\mu\nu}\chi_\mu, \quad (2.01)$$

the new energy parameters  $e_{\nu\mu}$  now replacing the  $E_{nm}$  set. There is a simple relation between the two sets of energy parameters. If the relation between the  $(\chi)$  orbitals and the  $(\psi)$  orbitals is given by

$$(\chi) = T(\psi), \quad T = (t), \quad (2.02)$$

where  $T$  is some transformation operator, represented by the matrix  $(t)$ , then

$$e_{\nu\mu} = \sum_m (\bar{t}_{\nu m} t_{\mu m}) E_{mm}. \quad (2.03)$$

Similarly if the  $e_{\nu\mu}$  should be known, the values of  $E_{mm}$  can be obtained from relations of an inverse type, viz.,

$$E_{mm} = \sum_{\mu, \nu} (t_{\mu m} \bar{t}_{\nu m}) e_{\mu\nu}. \quad (2.04)$$

An orbital set of great value in discussing molecular structure is that which gives the maximum degree of equivalence among the members of the set. Thus in a molecule with tetrahedral symmetry, as in methane, a set of molecular orbitals can be superimposed, as indicated by equation (2.02), so as to produce four orbitals which are equivalent. They are equivalent in the sense that the distribution appropriate to one orbital is identical with that of another except for its orientation in space. Now it follows from equation (2.01), using the orthogonal property of the  $\chi$ -orbitals, that

$$e_{\nu\mu} = \int \bar{\chi}_\nu (H + V + A) \chi_\mu dx. \quad (2.05)$$

Certain simple relations between the  $e_{\nu\mu}$  parameters follow for equivalent orbitals. Thus suppose that  $\chi_1$ ,  $\chi_2$ ,  $\chi_3$ , and  $\chi_4$  are four equivalent orbitals in methane, the relative orientations being those of four tetrahedral directions, then the diagonal elements of the  $(e)$  matrix have the same value, say  $a$ , and the off diagonal elements have the same value, say  $b$ . The  $\chi$ -orbitals of methane arise from four molecular orbitals, three of which have the same energy. There are thus two energy parameters  $E_{1,1}$  and  $E_{2,2}$ , one being the ionization potential from a completely symmetrical orbital, and the other from one of three orbitals with the same energy. The relation between these quantities and  $a$  and  $b$  is [Lennard-Jones (4)],

$$\frac{1}{2}(E_{11} + 3E_{22}) = a, \quad \frac{1}{2}(E_{11} - E_{22}) = b. \quad (2.06)$$

The equivalent orbitals may be regarded as generalizations of those directed atomic functions, which are usually called hybridized atomic orbitals. Like the latter they often have directional properties. They are more localized than molecular orbitals; in fact, electrons assigned to them may be said to "correspond" to the chemist's notion of a chemical bond. (In some cases they may correspond likewise to lone pairs of electrons, or even to inner electrons which do not directly take part in molecular formation.)

Equivalent orbitals associated with particular bonds may not change very much from one molecule to another if the environment of the bond is similar. Thus the equivalent orbitals associated with the CH bonds in a long hydrocarbon may be much the same except for those near the extremities. The same remark applies to the CC bonds. For this reason the same  $e_{\mu\nu}$  parameters may be associated with the bonds emanating from each carbon atom. Moreover, these quantities may be taken to be the same for the same groups in other molecules. Without knowing or specifying the  $\chi$ -orbitals it is possible to use them as a basis for the discussion of the properties of related molecules. Thus the ionization potentials  $E_{nn}$  are obtained by solving the equation

$$|\epsilon - E(1)| = 0 \quad (2.07)$$

and then the molecular orbitals, being expressed as a linear sum of the  $\chi$ 's in the form

$$\psi_n = \sum_r \bar{t}_{rn} \chi_r, \quad (2.08)$$

are obtained by solving the equations

$$\sum_r (e_{\mu\nu} - E_n \delta_{\mu\nu}) \bar{t}_{rn} = 0. \quad (2.09)$$

The process is thus similar to that of the familiar secular equation, but the eigenvalues here are identified with ionization potentials.

Hall (14) has used this method to discuss the ionization potentials of related sets of molecules. He has shown that the ionization potentials of the hydrocarbon series from propane to decane can be correlated by a suitable choice of the parameters  $e_{\mu\nu}$ . Thus the value of  $e_{\nu\nu}$  for a CC bond was taken to be  $-13.24$  ev., the value of  $e_{\mu\nu}$  for two neighboring CC bonds  $-1.48$  ev. Such quantities may be found to provide useful information about the properties of bonds in molecules. They are derived from ionization potentials and not from thermochemical data, the source of most theoretical information about molecules up to now. Perhaps the most significant aspect of this theory is that it has opened up a new method of investigating the electronic structure of saturated molecules. Many of the properties of such molecules are known to be nearly additive and depend only on the number of bonds. Thus the total energy, diamagnetic susceptibilities, and polarizabilities may often be expressed in terms of characteristic bond properties. [Hall (18)].



A further development of this work has been made by Lennard-Jones & Hall (15), who have considered the distribution of positive charge caused by the removal of an electron. The process of ionization, whereby an electron is removed from a molecular orbital, may be interpreted as the removal of an electron with varying degrees of probability from the equivalent orbitals, or, more loosely, from the various chemical bonds. These probabilities may be expressed in terms of the coefficients  $t_{nv}$  in equation (2.08). The ionization of normal octane has been worked out in detail from this point of view. This type of calculation may help in the elucidation of the process of dissociation which often follows ionization by electron impact.

*Properties of conjugated molecules.*—The theory outlined above has to be modified when applied to conjugated molecules. Usually for the ground states of such molecules and also for low excited states the  $\pi$ -electrons do not completely fill a set of associated molecular orbitals. In the ground state of benzene, for example, the six  $\pi$ -electrons occupy only three of the low molecular orbitals, and there are three others unoccupied. This is analogous to the band theory of simple metallic conductors. The electrons occupy only the lower half of a band. As a result of this it is not possible to transform the occupied molecular orbitals into equivalent orbitals, which are localized on one atom or in one bond. This difficulty was discussed by Hall & Lennard-Jones (16) with reference to butadiene and benzene.

To overcome this difficulty a modified method has been proposed by Hall (17). He supposes that there is some form of equivalent orbital of  $\pi$ -symmetry, associated with each carbon center, which is localized, though the orbital does not necessarily coincide in distribution with an atomic  $p\pi$  orbital of the hydrogen type. In terms of this a set of molecular orbitals can be obtained by linear combination, and these have the orthonorm property. Conversely, if a set of molecular orbitals is assumed known, then the equivalent orbitals can be derived by an inverse transformation. If the set of molecular orbitals were each occupied by an electron of the same spin, then the determinantal form of the wave function would not be altered by an orthonorm transform which associates each electron of the same spin with an equivalent orbital distributed about each centre. These equivalent orbitals, which need not be precisely defined, are used as a basis for calculation, and physical quantities can be expressed in terms of them.

Hall (17) has shown that the more bonding half of the molecular orbitals obtained from the equivalent orbitals satisfy equations of such a form that they are nearly the same as the equations satisfied by those molecular orbitals which are occupied in the ground state. Hall assumes them to be the same and shows how the method used for saturated molecules may then be extended to conjugated molecules. The method involved some approximations, but corrections can be found to allow for these. For some molecules (alternant hydrocarbons) many corrections vanish. Hall has shown how by his method the ionization potentials not only of conjugated hydrocarbons but

also of heterocyclic compounds might be calculated or, alternatively, used to yield information about equivalent orbitals.

Perhaps the most interesting application of this theory has been to discuss the total energies of conjugated molecules [Hall (18)]. It is possible to compute the resonance energies of conjugated molecules, particularly conjugated hydrocarbons, by a method which superficially resembles that of the "linear combinations of atomic orbitals" method. The method is fundamentally different, however, since nothing is defined in the same way. It appears, nevertheless, that when the parameters of both methods are determined by comparison with experiment they will yield the same results for hydrocarbons but not for heteronuclear molecules. This suggests that the successful application in the past of the method of linear combination of atomic orbitals to conjugated molecules has been due to its coincidence with this more accurate theory. This suggestion is strongly supported by the evidence on excited states. The lowest triplet state of an alternant hydrocarbon<sup>3</sup> is easily calculated by this method. Both this quantity and the resonance energy can be expressed as multiples of a single parameter  $\beta$ . The values of this parameter, which successfully correlate calculation with observation, prove to be approximately the same whether obtained from spectroscopic evidence or from resonance data. Hitherto widely different values of  $\beta$  have had to be used for the two sets of observational material. A discussion of the relation of this method of approach to the more conventional one (that is, the linear combination of atomic orbitals) has been given by Lennard-Jones & Hall (19).

The same kind of explanation has now been given by Dewar & Longuet-Higgins (20) of the practical success of the resonance theory applied to alternant hydrocarbons despite the errors in the assumptions on which it is usually thought to be based. They show that, if the determinantal equations of molecular orbital theory are solved by a perturbation method, the results are closely parallel to those of resonance theory. Thus the molecular orbital bond order may be found approximately by the procedure for finding the double bond character from the unexcited classical structures. Similarly the rules for the stability and reactivity of these molecules can be justified though with some exceptions.

It appears, therefore, that the empirical success of what had been thought to be independent methods of investigating conjugated hydrocarbons may be attributed to the close parallelism between the equations which they use and not to the validity of the assumptions on which they are based.

*Chemical properties and absorption spectra of conjugated molecules.*—A

<sup>3</sup> For certain conjugated hydrocarbons, the carbons can be divided into two sets, no member of which has a near neighbour of its own kind. These are called alternant hydrocarbons.

simpler but less accurate method of dealing with conjugated molecules has recently been used by Dewar (21). It aims at correlating their chemical and spectroscopic properties, but, in view of the assumptions made, the theory cannot be expected to give more than a first approximation to the quantities calculated.

In the earlier part of this report it was pointed out that the solution of the wave equation (1) can be obtained in approximate form if the actual electrostatic forces acting on each electron are replaced by some suitable average, so that the potential field is a function only of three space co-ordinates. The type of solution was then given in equations (1.04) to (1.09). In this derivation it was supposed that the wave functions and energies of the one-electron wave equation (1.04) could be found. In the absence of such solutions a further approximation has had to be introduced into the theory in the past by assuming a particular form of solution. It has been usual to express these one-electron wave functions as linear combinations of atomic orbitals, there being one of these at each conjugating center. For  $N$  centers

$$\psi_j = \sum_{r=1}^N a_{jr} \zeta_r, \quad (2.10)$$

where the  $\zeta_r$  are atomic orbitals. They are usually regarded as  $2p\pi$  orbitals, but their detailed specification is not required except that they are always taken in real form. They are normalized, but not orthogonal to each other. This non-orthogonality is neglected in the theory, the  $\psi$ 's being taken as orthonorm transforms of the  $\zeta$ 's, these being assumed to be an orthonorm set. Since the Hamiltonian is assumed to be separable in the co-ordinates of each electron, the energies appropriate to the  $\psi$ 's are given by

$$\epsilon_j = \int \psi_j H \psi_j dv, \quad (2.11)$$

where  $H$  is the effective Hamiltonian. The total energy is then given by equation (1.08) above.

The equations determining the coefficients of the atomic orbitals in  $\psi_j$  are

$$\sum_{s \neq r} a_{js} \beta_{rs} = (\epsilon_j - \alpha_j) a_{jr} \quad (r = 1, 2, \dots, N) \quad (2.12)$$

where

$$\beta_{rs} = \int \zeta_r H \zeta_s dv, \quad \alpha_r = \int \zeta_r H \zeta_r dv. \quad (2.13)$$

The quantity  $\beta_{rs}$  is called the resonance integral and is assumed to be zero except when  $r$  and  $s$  are nearest neighbours. The Coulomb integral  $\alpha_r$  is usually included in  $\epsilon$  for hydrocarbons, energy changes thus being referred to  $\alpha_r$  for carbon. For alternant hydrocarbon molecules with an odd number of carbons, there is one wave function  $\psi_j$  for which the energy  $\epsilon_j$  is zero rela-

tive to the Coulomb energy  $\alpha_j$  for a carbon atom. As Longuet-Higgins (22) has pointed out, the secular equations take for this orbital a simple form, viz.

$$\sum_{s \neq r} a_{js} \beta_{rs} = 0 \quad (r=1, 2, \dots, N). \quad (2.14)$$

Further, the values of  $\beta_{rs}$  are equal when the distance between neighbors is the same, so that the  $\beta$  factors drop out and the last equation gives a simple relation between coefficients. In an odd alternant hydrocarbon the coefficients  $a_{js}$  for the carbon centres in the less numerous set turn out to be zero for the nonbonding orbital. The above relation then implies that for those centres which are nearest neighbours of any particular carbon atom the sum of the coefficients is zero. This provides an easy method of evaluating the ratio of the coefficients and the normalization condition then fixes all of them.

The aim of the approximate methods introduced by Dewar (21) is to relate the absorption spectra of conjugated hydrocarbons and their chemical derivatives to the properties of nonbonding orbitals. Suppose, for example, that RS represents an even alternant hydrocarbon, which can be regarded as made up of two odd alternant hydrocarbons R and S. Then R and S, when separated, will each have a nonbonding orbital and each will be singly occupied. When R and S interact the nonbonding orbitals will split into a bonding orbital and an antibonding orbital, the energy of the one being lower by an amount  $\epsilon$  than the nonbonding orbital, the energy of the other being raised by the same amount. In the ground state of RS the lower of these two orbitals will be doubly occupied and the upper one unoccupied. The energy required to excite an electron from the one to the other will be  $2\epsilon$ . If  $a_{0r}$  and  $b_{0s}$  are the coefficients of the nonbonding orbitals for the terminal atoms of R and S, then the quantity  $\epsilon$  is given simply by

$$\epsilon = \sum a_{0r} b_{0s} \beta, \quad (2.15)$$

where  $\beta$  is the resonance integral for a C—C bond, and the summation is over those (conjugated) bonds which join R and S. Hence the longest wave length of the absorption spectrum should be given by

$$\lambda_0 = C(\sum a_{0r} b_{0s})^{-1} \quad (2.16)$$

where  $C$  is some constant to be determined empirically. The determination of this constant presents some difficulty, for the excitation of a single electron leads to both singlet and triplet states, which may differ considerably in energy but are not distinguished by the one-electron method of approximation. Dewar suggests ways of overcoming this difficulty. He is able to calculate  $\lambda_0$  for a large number of hydrocarbons and obtains fair agreement with experiment.

Similar ideas have been applied by Dewar (23) to calculate the chemical properties of conjugated molecules. Most of the results in these papers are

new, but some theorems of other authors have been included so as to make the presentation of the theory self-contained. Thus the formula for  $\epsilon$  above, equation (2.15), can be used to estimate the resonance energy of an even alternant hydrocarbon RS. The idea is that this quantity arises mainly from the interaction of the singly occupied nonbonding orbitals of two radicals R and S, the interaction of all the doubly occupied orbitals in R and S being such as to give little net gain of energy when the molecule RS is formed.

Aromatic hydrocarbon derivatives are treated as perturbations of the corresponding isoelectronic hydrocarbons or hydrocarbon ions. Hetero-aromatics are dealt with by partitioning the molecule into an odd alternant hydrocarbon R and a hetero-atom S, interaction between the nonbonding orbital R and the atomic orbital S being calculated by approximate methods. The problem of substitution is considered and the conclusion reached that the only valid method is to calculate the energy of the transition state, as has been done by Wheland (24), whereby a carbon atom undergoing substitution is assumed to be in a state of  $sp^3$  hybridization and so removed from conjugation. Assuming that this contribution to the transition state is the same for all positions in the molecule, it only remains to calculate the energy of the mobile electrons for the atoms still in conjugation in each case. Substitution should be most rapid at the position for which this energy is lowest. The results are found to be in general agreement with experiment, particularly for hydrocarbons.

The methods used by Dewar provide a quick and simple way of predicting the chemical properties of conjugated molecules, particularly of hydrocarbons, but the application to hydrocarbon derivatives with hetero-atoms or polar substituent groups is less reliable. For such molecules the derivation of simple formulae involves drastic approximations or, alternatively, extensive corrections are necessary and these destroy their semi-quantitative value.

*Molecular compounds and their spectra.*—It is well known that the mixing of two colourless or nearly colourless organic compounds sometimes produces strong colour. This may be taken as evidence of the formation of complexes between the participating molecules. In an interesting and important series of papers, Mulliken (25, 26, 27, 28) has discussed the nature of the interaction which leads to complexes of this type and to the type of electron transition which produces colour. In so doing Mulliken was led to an examination of compounds (AD) formed by the combination of electron donors (D) and acceptors (A) and to a discussion of their properties. In quantum mechanical language the wave function of such a compound is expressed approximately in the form

$$\psi = a\psi_0(AD) + b\psi_1(A^-D^+),$$

the functions  $\psi_0$  and  $\psi_1$  corresponding respectively to some form of interaction between A and D alone, and between  $A^-$  and  $D^+$  alone, the interaction in

each case depending on the structure of A and D. The equation represents a superposition of idealized states or "structures" and implies a partial transfer of an electron from D to A. The definitions of acceptor and donor set out by Mulliken include the use of such terms for Lewis acids and bases and also for reducing agents and oxidizing agents. They also provide for transfers of electrons of the  $\sigma$  and  $\pi$  types not only from atom to atom but also from molecular groups to other molecular groups. The concept of electrons occupying molecular orbitals associated with groups forms a convenient mode of description for such complexes.

It is possible to describe excited states of complexes by a wave function of the above type. [There must, for example, be at least one such which can be expressed as a linear sum of  $\psi_0(AD)$  and  $\psi_1(A^-D^+)$ .] The usual perturbation methods yield formulae for the energy of transition from ground state to excited state, and the intensity of transition can be related to the matrix elements of the electron displacement (the dipole vectors) in the usual way. The observed intense absorption of the benzene-iodine complex in the region of  $\lambda$  2900 can thus be qualitatively explained. The properties of compounds of the  $BX_3 \cdot NR_3$  type and complexes formed by an ion such as  $Ag^+$  with conjugated systems, such as ethylene or benzene, can be similarly interpreted.

#### SPATIAL CORRELATION OF ELECTRONS IN MOLECULES

Chemical change is usually accompanied by the release or absorption of energy. For this reason calculations of energy changes are of primary importance in theoretical chemistry. It thus becomes necessary to calculate the energy content of molecules. By this is meant the energy required to separate the electrons and nuclei which make up a molecule. For a fixed arrangement of nuclei this quantity can be expressed as the sum of four parts. There is, firstly, the average potential energy of the electrons in the presence of the nuclei; secondly, the potential energy of the nuclei in the field of each other; thirdly, the average kinetic energy of the electrons; and, finally, the average potential energy of the electrons due to their mutual electrostatic forces. Of these the fourth is the most difficult to calculate because it depends on the average arrangement of the electrons relative to one another. The average distribution (or atmosphere) of electrons around any one electron will depend as a rule on the position of that electron. The distribution is thus a function of six dimensions. It is the difficulty of finding such a function for electrons in molecules which holds up progress. The central problem of molecular theory is how best to determine the spatial correlation of the electrons.

There are two major factors which determine spatial correlation. One is the exclusion principle and the other is the electrostatic repulsion of the electrons. Of the two the first of these is often the more important. It is strikingly effective between electrons of the same spin. For this reason this factor will be considered first.

*Spatial correlation of electrons of the same spin.*—Both the molecular orbital theory and the electron pair theory make full use of the exclusion principle by making the complete wave function antisymmetrical. In the molecular orbital theory, as described in the first section, the orbitals are orthogonal to each other, either in virtue of their spatial properties or because of their spin factors. In the electron pair method only the orbitals on the same atom are orthogonal. Orbitals on different atoms are not orthogonal except when the atoms are infinitely separated. If orbitals are used from different atoms at finite separation to construct a wave function for a bond, they are not as a rule orthogonal.

Orthogonal and normalized orbitals, as used for molecules or for separated atoms, form the basis of the theory of directed valency. An atom such as carbon in its  $^3S$  state, for example, can be represented by a determinantal wave function, in which the component orbitals are  $s$  and  $p$  functions. Such a wave function automatically results in spatial correlation of the electrons of the same spin. It appears from the work of Artmann (29), Zimmerman & Van Rysselberghe (30) and Linnett & Poë (31) that in multidimensional space the wave function has a maximum, and the maximum corresponds to that configuration of the electrons in ordinary space for which the vectors joining the electrons to the nucleus are inclined to each other in a particular way. For carbon these vectors are along tetrahedral directions. The antisymmetry condition, which, for electrons of like spin, means antisymmetry in space co-ordinates, has the effect of keeping the electrons apart. It is thus a potent influence in determining the structure of atoms and of still greater significance in determining molecular shape.

The spatial correlation of electrons of the same spin in atoms and molecules has been discussed by Lennard-Jones (32). For closed shells of inert-gas-like atoms there is a correlation of the  $\alpha$  spin electrons among themselves and a similar correlation of the  $\beta$  spin electrons among themselves, but a simple determinantal function provides no correlation between electrons of opposite spins. The electrons of the same spin tend to dispose themselves in tetrahedral directions. If the exclusion principle were the only factor influencing spatial correlation, the two tetrahedra would move independently of one another. There is, however, the effect of electrostatic repulsion between electrons of unlike spins and this must tend to keep the two tetrahedra apart. Improvements in the form of the wave function must be introduced if this is to be taken adequately into account. Similarly in molecules with triple bonds, as in  $N_2$  and  $C_2H_2$ , the simple molecular orbital picture suggests that the electrons of the same spin tend to arrange themselves in azimuthal planes making an angle of  $120^\circ$  with each other, but to the first approximation the set of electrons of one kind of spin is not correlated with the set of electrons of the other kind of spin (32).

The electron pair theory also uses correlation of electrons of like spin but in rather a different way. Since it is based on the properties of atoms at



an infinite distance from each other, the correlation is restricted to that of electrons of the same spin on the same atom. The method of superposition of atomic wave functions to give new wave functions with directed properties (the so-called hybridized orbitals) was in essence a means of providing spatial correlation of electrons of the same spin, before the atom was brought into interaction with other atoms. This is the reason for the success of the method of hybridization, as first used by Pauling (33) and Slater (34).

The discussion of spatial correlation so far has been concerned with molecules in their ground states, for which the electrons are paired in orbitals of the lowest available energy, but similar considerations can apply also to some of the excited states. The easiest to deal with are those in which some of the outer electrons are unpaired but have the same spin. The wave functions for such states can, as a rule, be expressed also as single determinants, and, for the reasons already given, the spatial correlation of the electrons, particularly of the outer ones of the same spin, automatically introduced by such a wave form, should render the calculations of the energy a good first approximation. Other excited states, which are degenerate because of the different ways of assigning the outer electrons to available orbitals, cannot be dealt with in so straightforward a way. It is necessary to take sums of determinants for the wave function, and this, as a rule, implies that electrons are being paired in different ways. The antisymmetry condition does not then lead to the same degree of spatial correlation and calculations of the energies of such states will be less reliable. It is then that the theory runs into the major difficulty of finding out the effect of electrostatic forces on the spatial correlation of electrons of opposite spin.

*The pursuit of  $1/r_{12}$  (two-electron systems).*—It remains one of the basic problems of molecular theory to devise simple but accurate wave functions which reflect the tendency of the electrons to avoid each other owing to their mutual repulsions. Because of the great importance of this aspect of the theory there has been a tendency to return to the study of simple systems, not because of their intrinsic interest but because methods of solution devised for them might lend themselves to wider application. It is doubtless for this reason that work on the two-electron systems of helium and hydrogen has been renewed. Though Hylleraas (35) as long ago as 1930 obtained as near an approximation to the wave function of the ground state of the helium atom as is ever likely to be achieved, the method of deriving it and the analytical form in which it was expressed do not permit an extension to more general systems. Taylor & Parr (36) have shown that a very good approximation to the total energy can be obtained by expressing the wave function as a sum of component parts which can be denoted symbolically by  $(1s1s')$ ,  $(2p)^2$ ,  $(3d)^2$  and  $(4f)^2$ . The calculated total energy in atomic units proves to be 5.79486, which differs from the experimental value by only 0.0117, an error of only about 0.02 per cent. The Hartree-Fock representation of the  $(1s)^2$  type involves an error of nearly seven times as much. It is evident



from the form of the wave function that there is a radial correlation and an angular correlation; one electron may tend to be "out" when the other is "in," and again electrons may tend on the average to subtend at the nucleus an angle greater than  $90^\circ$  (the uncorrelated average).

Mulliken (37) has given a similar discussion of possible ways of improving the calculated value of the energy of the helium atom by taking various configurations into account and has carried out a parallel examination of the problem of the hydrogen molecule. This he considers from the point of view of molecular orbitals and from that of the Heitler-London approach. He suggests, for example, that for the hydrogen molecule the natural generalization of the simple molecular orbital representation  $(\sigma_g)^2$ , where  $\sigma_g$  denotes as usual a symmetrical orbital about both centers, is to take a summation of the type

$$\sum a_i(\sigma_{gi})^2 + \sum b_i(\sigma_{ui})^2, \quad (3.01)$$

where  $\sigma_{gi}$  denotes a typical member of the sequence of symmetrical two center orbitals and  $\sigma_{ui}$  a similar member of the antisymmetrical set. This process would correspond to what has been called in-out correlation in the case of the helium atom and also to correlation about the midplane of symmetry. When one electron is on one side of the midplane, the other will tend to be on the opposite side because of the mutual repulsion between them and the disposition of the nuclear field.

In order to find a physical basis for the choice of configurations in such a problem, Lennard-Jones (38) has reported a fresh analysis of the wave equation of the two-electron problems of helium and hydrogen. Since  $1/r_{12}$  can be expanded as a series of spherical harmonics in  $\theta_{12}$ , it was proposed that the wave function should be expressed in the form

$$\psi(1, 2) = \sum_n \psi_n(1, 2) P_n(\cos \theta_{12}). \quad (3.02)$$

This, when substituted in the wave equation, led to a series of terms each containing the same Legendre function, so that owing to the different symmetry properties in  $\theta_{12}$  they could each be separately equated to zero. In this way a set of coupled equations for the functions  $\psi_n(1, 2)$  was obtained. This provides a formally exact solution of the helium problem. The calculations of Taylor & Parr (36) fall within this scheme, though with the simplification that all of their functions of the radial co-ordinates are expressed as hydrogenlike functions with appropriate values of  $Z$ , the effective nuclear charge. The successive terms in the expansion correspond exactly to the expansion (3.02) above. It is gratifying to find that, even with the limitation in the form of the radial functions, four terms in the expansion suffice to give a remarkably good approximation to the energy. A fuller discussion of the helium problem has been given by Lennard-Jones & Pople (39).

Just as Hylleraas provided a solution of the helium problem by the use of the co-ordinate  $r_{12}$  in the wave function and the application of the vari-

ational method, so James & Coolidge (40) produced the most accurate wave function and energy of the hydrogen molecule that has yet been given. Unfortunately the method does not lend itself to generalization. In order to investigate the correlation of paired electrons in a bond, Lennard-Jones & Pople (38, 41) examined the properties of the wave equation for the hydrogen molecule and used the von Neumann expansion for the  $1/r_{12}$  term in elliptical co-ordinates  $\xi_1, \xi_2, \eta_1, \eta_2$  and the angle  $\phi_{12}$ . It was then shown that the wave function for the ground state of symmetry  $^1\Sigma_g$  could be expressed accurately in the form

$$\psi(1, 2) = \sum_{m=0}^{\infty} (\psi_{s,m} + \psi_{a,m}) \cos m\phi_{12}, \quad (3.03)$$

where  $\psi_{s,m}$  and  $\psi_{a,m}$  are each functions of the co-ordinates  $\xi_1, \xi_2, \eta_1$  and  $\eta_2$ , the one being symmetrical in  $\eta_1$  and  $\eta_2$  and the other antisymmetrical in each. By separating out the terms arising from  $(1/r_{12})\psi(1, 2)$  into their various symmetry types a set of coupled differential equations was obtained from the wave equation for the set of functions  $\psi_{s,m}$  and  $\psi_{a,m}$  for all integral values of  $m$ .

Most of the forms proposed for the wave function of the hydrogen molecule can be expressed as a sum of terms of the type (3.03). Thus, the simple molecular orbital representation takes the form  $f_{s,o}(1)f_{s,o}(2)$ , where  $f_{s,o}$  is a function symmetrical about the midplane and does not involve  $\phi_{12}$ . This form is an approximation to  $\psi_{s,o}$ . It neglects the part which has symmetry  $\psi_{a,o}$  and neglects also all terms in the series which involve  $\phi_{12}$ ; that is, it neglects correlation about the midplane and correlation in azimuthal angle. Also by assuming a simple product of a function involving the co-ordinates of each electron separately, it neglects correlation of the "in-out" type. The form proposed by Mulliken (37), as given in equation (3.01) above, is an attempt to represent  $\psi_{s,o}(1, 2) + \psi_{a,o}(1, 2)$  by means of a superposition of configurations of the  $(\sigma)^2$  type.

A simple way of improving the molecular orbital configuration  $f_{s,o}(1)f_{s,o}(2)$  is to add a term to represent  $\psi_{a,o}$ . A suitable expression is  $f_{s,o}(1)f_{a,o}(2)$ , where  $f_{a,o}$  is a one-electron function independent of  $\phi$  and antisymmetrical in the midplane. If  $f_{a,o}$  is to be real everywhere, the approximation takes the form

$$\psi(1, 2) = f_{s,o}(1)f_{s,o}(2) - f_{a,o}(1)f_{a,o}(2). \quad (3.04)$$

The optimum expressions for  $f_{s,o}$  and  $f_{a,o}$  could be obtained by using equation (3.04) in a variational process to render the energy a minimum. Supposing this done, then by the transformation

$$\chi_A = (f_s + f_a)/\sqrt{2}, \quad \chi_B = (f_s - f_a)/\sqrt{2}, \quad (3.05)$$

the expression (3.04) becomes

$$\psi(1, 2) = \chi_A(1)\chi_B(2) + \chi_B(1)\chi_A(2). \quad (3.06)$$

This is a generalization of the Heitler-London formula, for the  $\chi$ 's represent optimum orbitals about each atom, but are derived from the molecular orbitals  $f_{a,o}$  and  $f_{a,e}$ . Equations (3.04) and (3.06) each ensures that there is some correlation of the electrons in the direction of the axis of the molecule. To obtain correlation in azimuthal angle as well it is necessary to generalize (3.04) and (3.06) so as to include similar terms with the factor  $\cos m \phi_{12}$ .

An analysis of recent calculations by Hirschfelder & Linnett (42) on the above basis has been carried out (41), and it has been demonstrated that when successive approximations are made to wave functions of the hydrogen molecule by taking in more terms of the type given in equation (3.03) the calculated average electrostatic interaction of the electrons becomes progressively less. A reduction in the calculated value of this quantity by as much as 33 kcal. is obtained. The significance of this inquiry lies in the importance it indicates of providing adequately for the correlation of paired electrons in bonds.

Present concern with the fundamentals of the theory was evident in the discussions at a conference on Quantum-Mechanical Methods in Valency Theory, held at Shelter Island, N.Y., U.S.A., in September 1951, of which a summary has been published (43).

*The pursuit of  $1/r_{12}$  (many-electron systems).*—With this general background it is profitable to examine some of the approximate methods which have been used to calculate the energies of the ground state and some of the low excited states of some molecules. The first attempt to apply both molecular orbitals and the Heitler-London method in an extensive way to complex molecules was made by Goeppert Mayer & Sklar (44) and by Sklar (45), but the results obtained for benzene were not altogether satisfactory.

It has since been recognised that the method, depending as it does on a simple configurational representation, is not sufficient and that, just as in the simple systems of the helium atom and the hydrogen molecule, discussed above, the interaction of other configurations of the same symmetry must be included. This generalization has been made by Parr & Crawford (46) for ethylene and by Parr, Craig & Ross (47) for benzene. Craig (48) has similarly carried out extensive calculations of cyclobutadiene and Coulson & Jacobs (49) of butadiene. The results obtained were disappointing, particularly for the higher electronic states, even though the wave functions were expressed as sums of determinants. This latter method is usually described as the calculation of configuration interaction.

Since, even with these improvements, the method has been found unsatisfactory, it has been suspected that there were systematic defects of a serious nature. Moffitt (50) has accordingly examined the theory by making a detailed comparison between the spectroscopic states calculated for the oxygen molecule and those observed. For this molecule there is sufficient information about the ground and low excited states to make a strict test of the value of such methods of calculation. The results of the calculation of

the ground state and four excited states yield a poor correspondence with the observed excited states when compared over the whole range of internuclear distances. Moffitt concludes that either the antisymmetrized molecular orbital approximation, using linear combinations of atomic orbitals, is quite inadequate to predict accurately the spectra of molecules, or its formulation contains serious deficiencies.

Moffitt finds that the asymptotic behaviour of simple wave functions (based on molecular orbitals) at large separation is incorrect. Thus the method indicates that the  $^3\Sigma_u$  state should separate into  $O^+$  and  $O^-$  ions, whereas observation indicates that the end products are an oxygen atom in its normal state ( $^3P$ ) and one in an excited state ( $^1D$ ). Similarly the calculated energy separation of the two states  $^3\Sigma_u^-$  and  $^3\Sigma_u^+$  as the nuclear distance becomes infinite is found to differ widely (by nearly 9 ev.) from that determined spectroscopically. The reason for this gross error is that the same atomic orbitals are used to describe not only a neutral oxygen atom, but also its positive and negative ions. What is more important is that the correlation energies are not correctly calculated by such an orbital description of the oxygen atom and its ions  $O^-$  and  $O^+$ . In other words the wave function used to calculate the energy of the molecule for small internuclear distances does not go over to a suitable form for large distances. Even if it correctly estimates the correlation energy for the molecule, it fails to give reliable values of the correlation energy for the constituent atoms.

Moffitt therefore suggests that this inadequacy of the theory for infinite separation should be accepted and that empirical steps should be taken to introduce the necessary correction. The system of infinitely separated atoms should be regarded as an unperturbed state, which is known from observation, and the interaction of the atoms at finite distances should be considered as a perturbation of that known state. Calculations of the energies of molecular states should not be looked upon as absolute but should be scaled up or down so that the calculated energy end-points (for infinite separation) coincide with atomic states, determined either by observation or by the use of more accurate atomic functions.

In a further paper Moffitt (51) has attempted to develop these ideas in a formal way. He attempts to separate the problem of finding the wave functions and energy level of atoms from that of finding their interaction. The chemist is interested in bond dissociation energies, the excitation states of molecules and the energies of activation of chemical reactions. These quantities are surface changes on a deep reservoir of energy. At present they have to be calculated as differences of large energy contents. Moffitt finds a form of representing the energy matrix of a molecular system as a sum of three parts. One of these refers to the system of separated atoms. This is to be obtained not by calculation but from atomic spectra. It contains the major part of the energy content of the system. The other two parts represent the interaction energy of the atoms in molecular formation

and the overlap of the wave functions of the atoms. For these last two contributions, it is suggested, approximate atomic wave functions may be used. Whether such a formal approach to molecular structure can be made to work in practice is a matter for future investigation, though as a physical picture it is attractive and promising.

*Approximate methods of calculating atomic and molecular wave functions.*—In a recent series of papers, Boys (52 to 56) has developed empirical methods of approximating the wave functions and energies of many-electron systems. The wave functions are expressed as linear sums of determinants, of which the component parts are products of simple exponential functions and spherical harmonics. It is stated that a complete set of theorems has been provided for the calculation of the coefficients of these expansions and that wave functions can be calculated to any degree of accuracy, provided relativistic effects are excluded. The only corresponding previous calculations of this type were those of Hylleraas (57) and these were restricted by the mathematical method to the two-electron problem of the helium type. This restriction to two electrons has now been removed by Boys, who has worked out wave functions for many of the atoms in the first short period, including the systems  $\text{Na}^+$ , Ne and  $\text{F}^-$ . In the process of calculation an impressive scheme of mathematical relations has been established for the calculation of matrix elements of the Hamiltonian and it is claimed that these can be expressed as a linear combination of one- and two-electron integrals.

In the calculation of molecular structure there has been an increasing tendency recently to use what Mulliken has described as "approximate theoretical methods" (58). In these methods approximate wave functions are used but exact computations are made of the integrals which occur. Kopineck (59) has published tables for two-centre integrals involving  $2s$  and  $2p$  atomic orbitals with the same effective nuclear charge. Barnett & Coulson (60) have also evaluated two-centre integrals involving equal and unequal nuclear charges. Mulliken, Rieke, Orloff & Orloff (61) have published tables of overlap integrals, and Roothaan (62) the values of one-electron integrals and two-electron Coulomb integrals. Tables of exchange integrals have also been given by Rüdénberg (63). Formulae for thirty integrals, involving  $2s$  and  $2p$  Slater atomic functions with unequal effective nuclear charges on two atoms have been worked out by Brennan & Mulligan (64). All the integrals are expressed in terms of natural logarithms, exponentials and exponential integrals. Extensive work is being done on the determination of such integrals and these form a necessary scaffolding for future constructive developments.

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# SPECTROSCOPY<sup>1</sup>

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To give a brief discursive review of all the original work published each year in the field of spectroscopy has now become an impossible task. The subject index of a single journal (*The Journal of Chemical Physics*) currently lists over 200 communications under the various subdivisions of "Spectra." Although the present article will be confined to vibration spectra, the author is still faced with the problem of deciding which contributions should be selected for comment, for selection is inevitable if the significance of the new work is to be made clear to the general reader. Fortunately, an excellent annual comprehensive review of the literature in infrared and Raman spectra is already well established. For each of the past three years Gore<sup>2</sup> (1) has collected and classified the growing output of papers in this field viz.: 274 in 1949, 354 in 1950, and 419 in 1951. The reader who wishes to know whether infrared (or Raman) spectroscopy has been applied to any specific problem may be safely referred to these admirable guides through what would otherwise be something of a jungle. Here we shall attempt to show the general pattern of current research using a representative selection of the published papers to illustrate the various trends.

## THEORY OF VIBRATION-ROTATION SPECTRA

The theoretical interpretation of the vibration-rotation spectra of polyatomic molecules in the gaseous state may be divided into three parts: (a) the assignment of the fundamental frequencies; (b) the explanation of the rotational fine structure of the individual absorption bands (leading to evaluation of the moments of inertia of the molecule); and (c) the correlation of the fundamental frequencies in terms of a potential function which will lead to meaningful values of force constants associated with changes in bond lengths and bond angles.

The assignment of fundamental frequencies in highly symmetrical molecules is done in two steps. First, the fundamentals are classified into groups according to their symmetry properties. Secondly, the fundamentals are assigned to the individual modes of vibration within each symmetry class, largely by means of semi-empirical rules concerning the relative and absolute magnitudes of different types of molecular vibrations. The theory of the first step has been established for some time (2); there is no exact theory of the second stage, since in a certain sense each molecule is a special problem. It will, therefore, be best to discuss any advances in this field in the sections which follow on individual molecules.

<sup>1</sup> The survey of the literature covering this review was concluded in January, 1953.

<sup>2</sup> The reviews by Dr. Gore contain several references to Raman spectra, but should not be regarded as comprehensive in this field.



Although the general principles governing the interpretation of the rotational fine structure of infrared and Raman spectra are well known, their detailed application to individual molecules cannot be carried out until a number of theoretical problems have been solved. This is especially true with regard to irregularities in fine structure arising from interaction between vibrational and rotational motions due to Coriolis forces. Perhaps the best known example of this kind of interaction occurs in certain bands of symmetrical top molecules. When the change of electric moment (associated with the vibration) is perpendicular to the symmetry axis of such a molecule, the spacing of the intense  $Q$  branches is given by

$$\Delta\nu = \frac{h}{4\pi^2} \left( \frac{1-\xi}{I_c} - \frac{1}{I_A} \right).$$

Here  $\xi$  is a factor which is different for each fundamental vibration. The individual  $\xi$ 's cannot be computed (without a complete knowledge of the internal force field) but the sum of the  $\xi$ 's for all of the fundamentals of this type has been computed in a few special cases. Lord & Merrifield (3) have now derived general rules for evaluating this sum in axially symmetric molecules of various symmetry classes. In general, the effects of Coriolis coupling are not so pronounced; the case just referred to is a special one arising from the identity of the two frequencies in a doubly degenerate fundamental. However, it may happen by accident that two fundamentals, between which Coriolis interaction can occur, have almost the same numerical value. In this case, the interaction markedly distorts the rotational fine structure of each band. This phenomenon was first studied in formaldehyde by Nielsen (4) who showed that it caused a decrease in certain spacings, where the two bands overlap and a corresponding increase in the outer wings of the two bands. The detailed explanation of a similar effect in allene has just been given by de Heer (5). A more complex type of anomaly, occurring in certain overtone bands of carbon dioxide where  $l$  type doubling is present in three levels coupled by Fermi resonance has been satisfactorily elucidated by deHeer & Nielsen (6). The highly irregular rotational fine structure associated with asymmetrical top molecules has always been especially hard to compute; a new method of calculating rotational line strengths in slightly asymmetric rotors (7), is therefore, of considerable interest.

In principle, the correlation of the fundamental vibration frequencies of a polyatomic molecule in terms of a potential function for the intramolecular force field may be done in two entirely different ways. In the first of these no assumption is made about the nature of the force field, except that it has the same symmetry as the molecule; in the second method, definite assumptions are made regarding the nature of the force field and means are sought of verifying these assumptions. The first method has two disadvantages: (a) the potential constants of such a field usually have no simple

physical interpretation, and (b) unless data are available on isotopic molecules, it is impossible to evaluate all the potential constants, since, in general, there are more such constants than there are frequencies from which to determine them. The second method suffers from neither of these particular disadvantages since (a) the potential constants are chosen to represent a force field of a definite type, and (b) by assuming that certain interactions are negligible, it is possible to reduce the number of unknown potential constants to be less than or (at the most) equal to the number of fundamental frequencies. The neglect of interaction terms may, however, be quite unjustified and the resulting picture of the force field in the molecule may be highly distorted. One way of deciding whether the interaction terms are really negligible is to assume that they do not vanish and then determine their magnitude by using data on isotopic molecules and possibly on Coriolis coupling constants. There are very few molecules for which the data are complete enough to allow this to be done. A recent addition to this list is ethane, for which Hansen & Dennison (8) have given a very detailed treatment. They first evaluated the 22 potential constants of a general potential function by using data on the frequencies and  $\xi$ -values in  $C_2H_6$  and  $C_2D_6$ . A transformation was then made to a valency force field containing all possible interaction terms. It turns out that the majority of the interaction terms are negligibly small with three exceptions, viz., interaction between (a) C—C stretching and C—C—H angle deformation; (b) C—H<sub>i</sub> stretching and H<sub>i-1</sub>CH<sub>i+1</sub> angle deformation; and (c) C—H<sub>i</sub> stretching and H<sub>i+1</sub>—C—C angle deformation. Furthermore, when comparison is made with a similar treatment given earlier for methane by Dennison (9) it is found that the principal force constants in the two molecules have very similar values and that the relative magnitudes of similar interaction terms run very parallel to one another.

As evidence of this kind accumulates, showing that the potential constants of certain groups (e.g., CH<sub>3</sub>, CH<sub>2</sub>, CCl<sub>2</sub>) vary very little in going from one molecule to another, it becomes possible to obtain the complete potential function for a variety of related molecules. This method has been very successfully exploited by Cleveland, Meister and their co-workers for halogen substituted methanes and ethanes (10, 11, 12, 13, 14).

The use of isotopic atoms as a means of determining the complete potential function for any molecule has been discussed in a very general manner by Decius (15) who has made his treatment specific for the case of linear molecules. He concludes that for a linear molecule ABCD . . . , it will be possible to obtain all the potential constants by studying isotopic molecules of the form A\*BCD, AB\*CD . . . , A\*B\*CD . . . , A\*B\*C\*D . . . , etc., and that more than two isotopic forms (such as A and A\*) of any given atom are not required. While it is interesting to see such general results worked out as an exercise in molecular vibration theory, the specific results needed for any present practical case can probably be obtained as readily

from first principles. It should also be remembered that it might be easier to use information from Coriolis coupling constants or closely related molecules than to obtain data on another isotopic species.

For some time there has been a puzzling anomaly about the force constants of diacetylene in that the stretching constant of the central C—C bond appeared to have a value around  $3.5 \times 10^6$  dynes/cm. This is markedly less than the normal value for a C—C single bond (approximately  $5 \times 10^6$  dynes/cm) whereas the anomalously low value of the bond distance would lead one to expect an exceptionally high value of the force constant. It has recently been shown (16, 17) by the discovery of a new Raman line that previous assignments were in error. A new assignment leads to a value of  $6.6 \times 10^6$  dynes/cm. for the force constant of the C—C bond in agreement with the short internuclear distance and the predictions of the resonance theory.

An interesting new development in this part of molecular physics is a calculation of the mean amplitudes of the thermal vibrations in  $\text{CF}_2=\text{CF}_2$  and  $\text{CH}_2=\text{CF}_2$ . This has been done by Morino, Kuchitsu & Shimanouchi (18) in order to compare the calculated amplitudes with values deduced from electron diffraction. The agreement obtained, although by no means perfect, is very encouraging. This should be a fruitful field for further work. Since the calculated amplitudes depend on the nature of the force field chosen, it may be that such a combination of electron diffraction and infrared techniques could eventually improve our knowledge of intramolecular force fields. Incidentally, the same authors (19) have pointed out that the amplitude of vibration of a bond length or of a bond angle is not necessarily a unique criterion for classifying fundamental vibrations as stretching, deformation, or rocking modes of particular bonds. At least in  $\text{CF}_2=\text{CF}_2$ , it is preferable to use the magnitude of the contribution made to the potential energy by the stretching of particular bonds or the deformation of particular angles. The general relations between the possible motions of the atoms in a triatomic molecule and the potential constants have been discussed very thoroughly by Torkington (20).

#### SMALL MOLECULES

Although papers have been published on the infrared and Raman spectra of hundreds of small molecules, the number for which reasonably complete and refined data are available is remarkably small, while the number for which a complete interpretation and analysis exists is distressingly small. The latter arises largely from difficulties encountered in interpreting the rotational fine structure of the nonlinear molecules. When this cannot be done, it may still be possible to make a fairly reliable assignment of fundamental frequencies but some doubt usually remains and, of course, no conclusions can be drawn about inter-nuclear distances. It is only during the past year that complexities in the rotational fine structure of certain infrared bands of

$\text{PH}_3$ ,  $\text{AsH}_3$  and  $\text{SbH}_3$  have been resolved by Nielsen (21), thus allowing accurate values to be obtained for the dimensions of these molecules. It is interesting to note that the bond angle is gradually approaching  $90^\circ$  as we pass from  $\text{PH}_3$  ( $93^\circ 50'$ ) to  $\text{SbH}_3$  ( $91^\circ 30'$ ) and that the dimensions derived from infrared data are in satisfactory agreement with those recently obtained in the microwave field (22). A new method of estimating the height of the potential barrier restricting inversion in  $\text{PH}_3$  and  $\text{AsH}_3$  has been proposed by Costain & Sutherland (23).

A small molecule which has given the spectroscopists a great deal of trouble is ozone. After oscillating between an acute and an obtuse-angled isosceles triangle for several years, the evidence recently became fairly conclusive in favor of the obtuse angle (24). A precise value of this angle has never been satisfactorily established from infrared data, but electron diffraction yielded a value of  $127^\circ$  (25). However, some recent microwave work (26) leads to a value of  $116.5$ – $117^\circ$  for the apical angle together with an O—O distance of  $1.276$ – $1.279$  Å. The rotational fine structure of the infrared spectrum has yet to be interpreted in detail and some recent theoretical work on the peculiar symmetry properties of ozone indicate a possibility that the ozone molecule is not exactly isosceles but only near-isosceles (27). It seems that the last word has yet to be said on ozone.

An excellent comprehensive review of the vibration spectra of unsaturated aliphatic hydrocarbons (acetylenes and olefins) has been given by Shepard & Simpson (28). A very noticeable feature in reviewing current work in vibration spectra is the great interest in halogenated hydrocarbons. This is probably because the investigation of series of related compounds of this type makes it possible to arrive at fairly satisfactory complete vibrational assignments and so to calculate thermodynamic functions. This has been done for many of the fluorinated ethylenes and ethanes (29, 30, 31) and halogenated methanes (32 to 39). Unusual small molecules which have recently been investigated include  $\text{NF}_3$  (40),  $\text{CF}_3\text{OF}$  (41) and the interhalogen compound  $\text{BrF}_3$  (42). The latter appears to be a tetragonal pyramid having  $\text{C}_{4v}$  symmetry.

#### INTENSITIES

Before 1946, relatively little attention was paid either to the accurate measurement or to the interpretation of the intensities of infrared and Raman vibration frequencies. From symmetry considerations, it is possible to predict whether any vibration frequency will have zero or nonzero intensity but nothing more. In order to predict the absolute intensity of a particular frequency in absorption (or scattering), it is necessary to be able to predict quantitatively how the dipole moment (or the polarizability) of the molecule is affected by that mode of vibration. The solution of this problem is still considerably beyond the scope of quantum mechanics in the case of polyatomic molecules, although some progress has been made for diatomic

molecules (43, 44). In the meantime, an experimental approach is being vigorously pursued in several laboratories by the accurate measurement of the absolute intensities of infrared absorption bands in simple polyatomic molecules. The stimulus for this development came from Wilson and his co-workers (45, 46), who showed that the absolute intensity of any fundamental band can be measured fairly easily by using pressure broadening to smear out the rotational fine structure. From such a measurement one obtains directly the value of  $(d\mu/dq)^2$  where  $\mu$  is the dipole moment of the molecule and  $q$  is the normal coordinate associated with that particular fundamental. If it is further assumed that each chemical bond (of length  $r$ ) has an effective bond moment  $\mu_b$  associated with it and that during molecular vibrations the effective charges move either along or perpendicular to the bond directions, it is usually possible (47) to determine the magnitude of  $\mu_b$  and  $d\mu_b/dr$  for the various bonds in the molecule. Unfortunately, the signs of these quantities cannot be determined, but by using isotopic molecules it may be possible to determine the relative signs of two bond moments. In this connection, Crawford (48) has recently derived a set of rules relating the intensities of corresponding bands in isotopic molecules, exactly analogous to the well-known Teller-Redlich product rules correlating the frequencies of isotopic molecules. Decius has given an additional relation (49) analogous to certain sum rules for isotopic frequencies derived recently by Decius & Wilson (50).

Using these methods, Hyde & Hornig (51) have shown from measurements on HCN and DCN that in these molecules  $\mu_{CH} = \pm 1.13$  D,  $\mu_{CN} = \pm 1.80$  D and that if C is positive in the CN dipole, then H is positive in the CH dipole. It is interesting to note how much less the effective moment of the CH bond is in methane (52, 53) where  $\mu_{CH} = \pm 0.31$  D. This is no doubt a consequence of the difference in hybridization of the  $s$  and  $p$  orbitals in the formation of these two different CH bonds. In the various methyl halides  $\mu_{CH}$  appears to have a fairly constant value near  $\pm 0.4$  D (54). However,  $d\mu_{CH}/dr$  changes uniformly in going from methyl fluoride ( $1.7 \times 10^{-10}$  D/Å) to methyl iodide ( $0.9 \times 10^{-10}$  D/Å). It must be emphasized that the reliability of values for effective bond moments and derivatives of bond moments is no greater than that of the potential functions used to correlate the fundamental frequencies. For small linear polyatomic molecules where complete potential functions have been determined, the bond moments have a very real significance. It will be much more difficult to obtain meaningful values as the work is extended to more complex molecules where the correct potential function is in doubt and the vibrational motions are not exactly along and perpendicular to chemical bonds.

What conclusions may be drawn from data of this type? Clearly the effective bond moment and its derivative are valuable additional characteristics of a chemical bond and can be used as a discriminant to indicate differences in bond character which may not be observable so easily by other means. Is it possible, however, to use this information to throw more light

on the electronic character of a chemical bond? Matossi (55) has derived relations between  $\mu$  and  $d\mu/dr$  for bonds and  $\alpha$ ,  $d\alpha/dr$  where the  $\alpha$ 's are atomic polarizabilities. The latter may be derived from observations on the absolute intensities of Raman frequencies (56). Using the data now available on NO, CO, CO<sub>2</sub>, N<sub>2</sub>O, CS<sub>2</sub>, COS, and C<sub>2</sub>N<sub>2</sub> he has attempted to verify these relations. The results are only moderately satisfactory indicating that the model (which is purely classical) is too simple. A more complex model has been put forward by Mecke (57) who formally analyzes the dipole moment of a bond into three components viz., ionic, polar, and inductive. Using a Morse function for the potential energy in an OH (or CH) group, Mecke is able to compute how these various components of the transition moment should vary in going from the fundamental vibration through the various overtones. Comparison of the predicted and observed variations leads to the conclusion that in the OH group the main contribution is from the ionic or polar terms, whereas in the CH group it is the inductive term which is predominant.

The enhancement of the absolute intensity of a vibration band of molecule A which occurs in the presence of high pressures of molecule B has been studied by Welsh, Crawford and their co-workers (58, 59, 60). Work of this kind is of considerable value because it provides a means of studying the distortion of the electron distribution of the absorbing molecule during collisions. Attention should also be drawn to the excellent work of Penner and his associates on rotational line intensities in vibration-rotation spectra and its application to the determination of flame temperatures (61, 62, 63). The measurement of absolute intensities of absorption bands in liquids has been investigated by Ramsay (64) and the method developed has then been applied to the identification of various CO groups in steroid molecules (65).

#### CRYSTALS

The vibration spectrum of a molecule in the gaseous state is governed by well defined selection rules. In the liquid state, there are no sharp selection rules, but in the crystalline state, the molecule is situated in a force field of a definite symmetry pattern and exact selection rules must again be in operation. Provided the crystal structure is known completely, it is possible to predict qualitatively (66, 67, 68) just how the absorption spectrum of a molecule changes in going from the gaseous to the crystalline state. As might be anticipated, degeneracies may be removed and combinations can occur between intramolecular vibrations and intermolecular lattice vibrations. However, single molecular frequencies may become multiple, the multiplicity depending on the number of molecules in the unit cell. The testing of these rules is now under way for a variety of small molecules and ions, e.g., CO<sub>2</sub> (69), NaNO<sub>2</sub> (70), and naphthalene (71).

In general, the agreement between prediction and observation is fairly satisfactory, but there are anomalies. There is a tendency at present to

attribute any bands which cannot be readily explained to "combination with a lattice mode" but, no doubt, more precise explanations will emerge as more work is done on a greater variety of molecules and ions, especially if it is extended to longer wavelengths where independent evidence can be obtained on the lattice vibrations. In the present state of development, it is not possible to use the vibration spectrum of a crystal as an independent means of determining crystal structure, but already infrared spectra are becoming a valuable supplement to x-ray diffraction spectra in the analysis of crystal structure. This is, of course, especially true with respect to the location of hydrogen atoms.

One of the difficulties in the interpretation of crystal spectra is how to distinguish between two different types of fine structure. A particular frequency may be split into two (or more) components either because a degeneracy has been removed by the crystalline field or because there are two (or more) molecules in the unit cell. A very neat way of overcoming this difficulty has recently been demonstrated (72, 73). The idea is to use a solid solution of a fully deuterated form of the molecule in an undeuterated form or vice versa. Thus, a certain band in crystalline deuterated naphthalene shows a doublet structure but when the deuterated naphthalene is diluted by 900 per cent of undeuterated naphthalene the band becomes single, showing that the splitting was due to intermolecular coupling between identical frequencies of two deuterated naphthalene molecules in the same unit cell. In an earlier version of the same idea, anthracene was used to dilute the naphthalene (74) but this is less satisfactory.

Although it has not been mentioned explicitly so far, it is obvious that in order to obtain the maximum amount of information from crystalline spectra, studies should be made on a single crystal, using plane polarized radiation incident at certain carefully chosen angles. There are considerable experimental difficulties in the way of this ideal program but a limited number of compounds have been investigated as single crystals or as arrays of single crystals similarly oriented. Aromatic compounds, such as substituted benzenes, are among the most suitable for work of this type and in certain cases conclusions may be drawn regarding the planarity of the molecule. Thus, Mann & Thompson (75) suggest that in dinitrobenzene, the nitro groups may be slightly twisted out of the plane of the aromatic ring; Francel (76) concludes that although *o*-nitrophenol, 2-nitroresorcinol and *o*-nitroaniline are planar, *o*-nitrobromobenzene and *o*-nitrochlorobenzene are nonplanar. Two other recent papers in this field which are of considerable general interest are concerned with a calculation of the normal frequencies of a simple cubic lattice (77) and a directional variation in the infrared reflection spectrum of quartz (78).

#### LARGE MOLECULES

The interpretation of the vibration spectra of large molecules is becoming increasingly important now that advances in infrared techniques are



making it possible to record the spectrum of almost any material (gaseous, liquid or solid) between  $4000\text{ cm}^{-1}$  and  $250\text{ cm}^{-1}$  in about an hour. The methods used for assigning frequencies in small molecules (based on analysis of rotational fine structure and on symmetry selection rules) are not applicable, since large molecules nearly always have to be examined in the condensed phase and in general have little or no symmetry. The usual approach to this problem is to investigate to what extent the fundamental frequencies of a large molecule may be separated into groups of fundamentals associated with smaller units vibrating more or less independently of one another within the molecule. It is an experimental fact that the vibration spectra of series of large molecules, having certain chemical groups in common, do exhibit common frequencies which can be reliably correlated with the fundamentals of such groups. The most recent collections of these correlations are contained in articles by Colthup (79) and McMurphy & Thornton (80). The former covers all types of molecules, while the latter is confined to hydrocarbons. The best established correlations are those associated with the stretching vibrations of OH, NH, CH, PH, SH, C=O, C=C, C=N, C $\equiv$ C and C $\equiv$ N bonds. Although there are many reliable correlations for the deformation frequencies of CH bonds (28, 80, 81, 82) there is often considerable uncertainty about the deformation frequencies of OH and NH bonds (83). It seems probable that hydrogenic deformation frequencies may occasionally interact with skeletal vibrations involving the stretching of C—C or C—N bonds (84, 85, 86). When this happens, it is no longer legitimate to regard them as separable and characteristic group frequencies. Such interaction effects can best be disclosed by studying the spectra of isotopic compounds. Thus, a separable hydrogenic deformation frequency in a hydrocarbon will be unaffected by the substitution of  $\text{C}^{13}$  for  $\text{C}^{12}$  and will, in general, be reduced by a factor close to  $\sqrt{2}$  when the hydrocarbon is deuterated. A new approach to the problem of calculating the fundamental frequencies of a large polyatomic molecule which has a low degree of symmetry has been outlined by Edgell & Riethof (87).

A systematic study of variations in the C=O frequency in about 80 compounds has been made by Josien & Fuson (88) and the changes observed have been correlated with environmental factors which might affect the electronic structure of the C=O bond. A study has been made of the infrared spectra of a large number of pyrimidines by Short & Thompson (89) and correlations discussed for characteristic frequencies of structural groups which differ in some respects from those reported earlier by Brownlie (90). The spectra of over 100 aromatic hydrocarbons (especially polycyclic) have been reported by Cannon & Sutherland (91), together with certain structural correlations.

The largest molecules being investigated by infrared methods are the proteins. Progress in this field prior to 1952 has been reviewed in a comprehensive article on the infrared spectra of amino acids, polypeptides, and proteins (92). One of the key problems is to determine the configuration of the



polypeptide chain in the  $\alpha$ - (or contracted) form of a fibrous protein. The model which currently seems to give best agreement with x-ray data is the Pauling-Corey helix (93). However, Mizushima & Shimanouchi (94) consider their infrared data favor an earlier model consisting of seven membered rings (95, 96). Elliott and his colleagues have pointed out that there are certain objections to the Pauling-Corey helix and have suggested a modification of it in order to account for the observed difference in the infrared dichroism of the NH and CO stretching vibrations in the  $\alpha$ -forms of oriented proteins and polypeptides (97). Fraser and Price favor the Pauling-Corey model and suggest the dichroic anomaly can be explained by other means (85). It is clear that more work is required before final conclusions on the structure of proteins can be drawn from infrared data. There are at present many unexplained features in the spectra of proteins (92) while the changes produced by deuteration, presence of ions, and variation of pH are also very puzzling (98, 99, 100). There are, however, some very suggestive resemblances between the changes occurring in the spectra of synthetic polypeptides as these go from the  $\alpha$  (folded) to the  $\beta$  (extended) form and the changes occurring in proteins during denaturation (101). Some evidence has also been obtained about the orientation of the CO and NH bonds in crystalline ribonuclease (102).

#### HYDROGEN BONDING

The existence of hydrogen bonding is probably most readily disclosed by its effects on vibration spectra. A review of the work in this field prior to 1952 has been given by Kellner (103) with particular reference to hydrogen bonding effects in molecules containing hydroxyl groups. The configuration of the  $\text{N}-\text{H} \cdots \text{O}$  group when hydrogen bonding occurs in amides has been discussed by Elliott (104). The extent to which this group of atoms can depart from a linear configuration is a matter of considerable importance in connection with models of protein structure. In this connection, the work of Mizushima and his colleagues on inter and intramolecular hydrogen bonding in amides is very important (105, 106). Hydrogen bonding effects on the NH stretching vibration have been detected in pyrrole and indole (107), thus throwing considerable doubt on a previous hypothesis (108) that there were two forms of these molecules. Similar results, although not so clear cut, were observed for aniline and diphenylamine. However, there still appear to be some unexplained features about the spectrum of pyrrole in the overtone region (109, 110, 111). Rundle & Parasol (112) have drawn attention to some exceptionally large shifts in the OH stretching frequency caused by hydrogen bonding and have proposed an empirical curve relating the OH frequency to the  $\text{O}-\text{H} \cdots \text{O}$  distance. Davies & Evans (113) have pointed out that the structure of the association band in solutions of certain amides and of trichloroacetic acid can apparently be accounted for in terms of sums and differences between the NH (or OH) stretching frequency and

low frequencies of the order of 70 to 200  $\text{cm}^{-1}$ . The latter are attributed to the associated molecules. Very little attention has been paid to the effect of hydrogen bonding on the deformation frequencies of OH and NH groups. Stuart & Sutherland (114) have shown that a broad diffuse band found near 650  $\text{cm}^{-1}$  in all alcohols in the associated state probably arises from the further restriction which hydrogen bonding imposes on the hindered rotation of the OH group. Detailed studies of the spectra of carboxylic acids in the free and in the associated state (deuterated and undeuterated) have thrown a great deal of light on the deformation frequencies of the OH groups in such molecules (115, 116).

#### DEVELOPMENTS IN TECHNIQUE

Improvements continue to be made in the technique of infrared spectroscopy and although none of them can be considered revolutionary, many are quite important for the solution of special problems. For instance, the average infrared prism spectrometer can resolve absorption maxima which are from 5 to 1.5  $\text{cm}^{-1}$  apart. While this is adequate for many purposes, there are occasions when higher resolving power is essential. A grating spectrometer will give an improvement by a factor of 10 but it is very expensive and has not the flexibility of a prism instrument. Moreover, it may be that a more moderate increase in resolution is all that is required. In such cases, Walsh and co-workers (117, 118) have shown that the resolution of a prism spectrometer may be increased by a factor varying from 1.5 to 3, by arranging matters so that the radiation makes four or more traversals of the dispersing prism. By this means, it should be possible to achieve a resolution of 1.5 to 0.5  $\text{cm}^{-1}$  in the range between 3500  $\text{cm}^{-1}$  and 250  $\text{cm}^{-1}$  provided the appropriate prisms are used for the various parts of this range. It should be noted that this gain in resolving power has not been achieved without certain drawbacks. It complicates very considerably the use of double beam methods to compensate for atmospheric and solvent absorption and, although a way of overcoming this has been suggested (119), all the multipass spectrometers so far reported are single beam instruments. Another disadvantage is that the chopping device which modulates the radiant energy stream falling on the detector must come after the absorption cell. This means that troubles may arise in examining the absorption spectra of heated samples; such troubles are normally avoided by having the chopper between the source and the absorption cell. On the other hand, one of the great virtues of the Walsh arrangement is that the purity of the spectrum at longer wavelengths is vastly proved by successive passes of the radiation through the prism. This is very important at all wavelengths beyond  $10\mu$ . The extension of the multiple pass idea to gratings has been made by several workers (120, 121, 122), while an ingenious combination of the multipass arrangement with a multislit device has just been proposed by Golay (123).

The limit to the resolution achieved by most infrared spectrometers

nearly always arises from the fact that the slit widths have to be kept large enough to allow a detectable amount of radiation to emerge from the exit slit. It follows that the performance of any spectrometer can be improved by providing it with a source of radiation more powerful than the traditional Nernst filament or Globar. Considerable progress has been made in this direction by using sources which operate at much higher temperatures than the Nernst filament (2200°K) or Globar (1400°K). The carbon arc, operating at 3900°K, was introduced by Strong and his associates (124, 125) and offers a very worthwhile improvement, but it is a cumbersome piece of equipment and increases the atmospheric absorption path very considerably. From the same laboratory has come a tungsten strip source (126) operating at 2900°K, which is from two to four times better than the Globar over the range 5 to 15 $\mu$  and is only worse than the carbon arc by a factor of two over the same range. Another scheme (127) has been to use the concentrated zirconium arc developed by Buckingham & Deibert (128). This operates at a temperature of at least 3000°K. and should give a performance very similar to that of the tungsten strip but no comparative figures are yet available. Mention should be made of a simple optical system recently described by Plyler & Kostowski (129) for increasing by a factor of about 3 the energy available at the entrance slit of the spectrometer from a flame source.

The only significant advance in the detector field is the discovery that thick layers of PbSe are photoconductive to wavelengths beyond 8 $\mu$  (130). This will provide a most valuable extension of the range of photoconductive detectors which was previously set at about 5 $\mu$  by lead telluride. A review of the main properties of the photoconductive detectors is now available (131).

A useful addition to the prism materials available for infrared spectroscopy comes from the development of suitable crystals of caesium bromide on a commercial scale. A prism of this material may be used to cover the range between 15 $\mu$  (limit of rock salt) and nearly 40 $\mu$  (132, 133, 134). Although the same long wavelength limit has been achieved with prisms of thallium-bromide-iodide, the latter material has serious defects in that it deforms very readily, has a very high refractive index, and is poisonous. Moreover, the dispersion of caesium bromide is considerably superior in the range between 15 and 28 $\mu$ , thus largely eliminating the need for prisms of potassium bromide. It seems possible that caesium iodide may become available in the not too distant future (135). It has been estimated that this would extend the range of observation to about 52 $\mu$ . Another potential addition to infrared prism materials is barium fluoride which transmits to slightly longer wavelengths than calcium fluoride (136). The additional range covered (about 2 $\mu$ ) is, however, not very significant, so unless it turns out to be much cheaper than the calcium salt, the advantages are not very apparent. Finally, attention should be drawn to the very interesting and useful properties of amorphous selenium as a lens (and even prism) material in the infrared (137).

A revival of interest in the techniques of the far infrared is reflected in

the appearance of several papers describing new instruments, constructed especially for use in the region between 25 and 1000 $\mu$ . Oetjen and his colleagues (138) have achieved excellent resolving power in the range between 40 and 150 $\mu$ ; McGubbin & Sinton (139) have obtained marked success in the virtually unexplored region between 150 and 700 $\mu$ , while Walsh (140) has proposed a zoneplate method which, if successful, may simplify the techniques in this region considerably.

The use of a reflecting microscope in conjunction with a micro-cell has been discussed by several workers (141, 142). It now appears to be feasible to obtain spectra from quantities of material of the order of a few micrograms dissolved in 4 to 50 times this amount of a suitable organic solvent. This opens up the possibility of studying the material obtained from paper chromatograms by infrared methods.

A valuable general paper on various very practical points in the technique of infrared spectroscopy (especially the construction of several types of absorption cell) has been published by Lord and his co-workers (143).

In the field of Raman spectra a full description has been given of a "Toronto type" source unit (144), and the potentialities of a spectrometer with a liquid prism have been investigated (145). The problem of measuring the intensities of Raman lines has been reexamined (146). The design factors in a photoelectric Raman spectrograph have been critically discussed by Busing (147).

#### ADDENDUM

The foregoing article was planned on the assumption that it need not be comprehensive. It now appears that the annual comprehensive review by Dr. R. C. Gore (1) is becoming biennial and will not appear until 1954. Under these circumstances, the author wishes to draw attention to a few other developments which should not go unnoticed.

These are (a) the renewed activity in the field of infrared emission spectra (148, 149, 150), (b) the development of work on rotational isomerism (151, 152), and the study of the structure of various metallic salts (153, 154) and inorganic ions (155).

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## CO-OPERATIVE ASPECTS OF PHASE TRANSITIONS<sup>1</sup>

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The problem of the explanation of phase transitions on a molecular basis is among the most challenging facing the present statistical theory of matter. The special value of a statistical theory is that in principle it can predict both the nature of the phases and of the phase transitions from molecular properties. Such a theory, even if not perfectly accurate quantitatively, is clearly more effective in advancing our understanding than a purely thermodynamical one where we must assume the existence and characteristics of the two phases *ab initio*. From the standpoint of statistical mechanics, phase transitions are generally regarded as the result of cooperative interaction between molecules, and the great difficulty in the field lies in the complexity of the mathematical description of the simultaneous cooperation of many molecules.

The first-order transitions where the energy and volume of the substance change discontinuously with the temperature and pressure are the best known experimentally, but the more subtle transitions, lambda points, Curie points, critical points, second- and third-order transitions, are more difficult to define experimentally and hence even more in need of theoretical investigation. Such questions as whether the specific heat is infinite at a point or finite but anomalous over a range or whether or not there is a small latent heat associated with the anomaly cause difficulty, as does also the much discussed question of the nature of the gas-liquid critical phenomenon. Most of this review is concerned with recent work on these and similar questions.

We have intentionally omitted more than passing reference to liquid helium, ferromagnetism, and superconductivity, since these are distinguished by quantum effects which would bring us into a new and difficult area of discussion. Lack of space prevents consideration of melting; the interested reader is referred to articles by Tisza, Mayer, Kirkwood & Rice in reference (101a).

### LATTICE THEORIES AND ORDER-DISORDER PHENOMENA

Much theoretical work has been done on the distribution of molecules over a lattice of points, with various types of interaction energy assumed. This idealized system is simpler than those in which the molecules are allowed to distribute continuously in space but it preserves many of the interesting features of real systems, including phase transitions of various types. A book by Guggenheim (37) appeared in the last year giving an excellent discussion of some of the theories of solutions from the lattice point of view.

<sup>1</sup> The survey of the literature pertaining to this review was concluded in January, 1953.

We shall review very briefly the nature of the several approximate theories. Most of these concern binary mixtures of two kinds of molecules, type A and type B. The energy of interaction of only pairs of nearest neighbors is usually considered. If the energy of the AB pairs is less than that of the AA and BB pairs the system tends to form a superlattice with A and B alternating in some regular fashion on the lattice points; if the energy of AB pairs is greater than that of the AA and BB pairs two phases, one rich in A and the other rich in B, tend to separate. Most authors have discussed one type of system or the other, but actually the theories of the two kinds of systems are closely related (37).

The simplest theories, called by Guggenheim the "zeroth-order approximation," assume that the distribution of molecules among the lattice sites is random despite the fact that the different configurations have different energy. Examples are the Hildebrand-Scatchard (42) theory of regular solutions and the Bragg-Williams (12) and Gorsky (35) theory of order-disorder phenomena.

Actually, the distribution will not be random if the energies of the different configurations are not the same. The quasi-chemical (25) and the Bethe (8) theories are two different "first-approximation" treatments of non-randomness leading to the same formulae. In both cases a simple approximate treatment is used for the probabilities of the various configurations, including Boltzmann weighting factors. Whereas the zeroth-order theories consider the distribution of single molecules, in the simplest and most common form of the quasi-chemical treatment the basic unit in which the configurations are described is the pair of molecules. Further improvements, at the cost of some complication, may be made by taking a triplet or quadruplet as the basic unit (39). Another method was suggested by Kirkwood (57). This consists of expanding the partition function in powers of reciprocal temperature. The coefficients of the first few powers are relatively easy to evaluate. The result turns out to be very similar to the quasi-chemical and Bethe result.

Another more general approach has been given by Kikuchi (56) in a recent important paper. His approach can become identical, by variation of parameters, with the first-approximation theory or with the more accurate "variation" theory of Kramers & Wannier (60). (The latter should not be confused with the exact theory of Kramers & Wannier mentioned below.) Kikuchi also treats three-dimensional lattices in detail. His method has been applied to two- and three-dimensional lattices of rotating dipoles by Oguchi (85) and Oguchi & Takagi (86).

To give an idea of the accuracy of the various theories, we compare them with the results of the exact calculation for the equimolar mixture on the square plane lattice discussed below. As the co-operative effects are introduced more adequately the transition temperature is lowered. The transition temperature is highest for the zeroth approximation, having the value  $4J/k$ , where  $J$  is defined below. The quasi-chemical approximation and the Kirk-

wood theory as far as it has been worked out give  $2.88(J/k)$  and  $2.78(J/k)$  respectively. The Kramers-Wannier "variation" theory (60) gives  $2.42(J/k)$ . The exact value is  $2.27(J/k)$ .

*Theory of the Ising two-dimensional lattice.*—The simplest lattice model that leads to phase transitions is a square net in a plane with coordination number four, the Ising lattice. This is also the most complicated system for which an exact statistical theory has been worked out, at least partially. With each lattice point is associated a variable that can take on two values, as for example, a spin that may be either plus or minus in the magnetic case or a molecule that may be either present or absent or of type A or B in the cases of the "lattice gas" or lattice solution respectively. The energy associated with a neighboring pair of sites is assumed to be  $+J$  if the pair is occupied in the same fashion but  $-J$  if it is occupied in unlike fashion. No other energies are assumed to be present.

Such a lattice was first used by Ising (48) for the discussion of ferromagnetism. He was able to treat a one-dimensional lattice (a row of points) exactly, but the results showed no phase transitions. A new and very powerful method was introduced by Kramers & Wannier (60) and independently by Lassetre & Howe (61). They observed that the new partition function resulting from a new atom being added to the lattice may be generated from the old partition function by a pair of linear algebraic equations. Associated with the whole set of linear equations that generates the complete partition function is a matrix algebra. The partition function may be obtained as the trace of a certain matrix, the trace being evaluated by solution of a characteristic value problem.

Kramers & Wannier did not themselves find the complete expression for the partition function, but they did obtain series for it useful at high and low temperatures. They also located the temperature of the Curie point together with some approximate values of the specific heat.

In one of the most remarkable papers of recent years, Onsager (87) obtained the accurate solution for the partition function at all temperatures by the use of a quaternion algebra, this probably being the only use of quaternions in twentieth-century physics. Later Kaufman (53) showed that the same operations could be more expeditiously performed by the use of spinor analysis, a generalization of the operations used to handle the electron spin in quantum mechanics [see also Kac & Ward (50)].

Kaufman & Onsager (54) obtained the partition function for the lattice with equal numbers of plus and minus spins (or equal numbers of A and B atoms). A single transition appears at a temperature  $T_c$  such that

$$\sinh 2J/kT_c = 1.$$

Long-range order exists below this transition but not above. In the neighborhood of the transition the molar heat capacity goes to infinity proportionately to the logarithm of  $(T - T_c)$ . This result is to be compared with the results of the various approximate theories mentioned above; in all of these

the heat capacity has a discontinuity but remains finite. The values of the transition temperature calculated by the various theories have already been given.

In the last year further advances have been made with this model. Lee & Yang (64, 114) calculated the spontaneous magnetization, or the composition and osmotic pressure of the two coexisting phases in the solution case, for the lattice below the critical temperature. We should point out here that the osmotic pressure of one of the components of a solution is equal to the total pressure of the corresponding lattice gas, which may be considered as a solution of molecules and holes. The mole fraction of the two coexisting phases is given by the expression,

$$N_i = 1/2 \pm 1/2[(1+x^2)(1-6x^2+x^4)^{1/2}/(1-x^2)^2]^{1/4}$$

where

$$x = \exp(-2J/kT).$$

The critical value of  $x$  is  $x_c = \sqrt{2} - 1$ . The mole fractions have a most remarkable behavior near the critical point, their difference approaching zero as the eighth root of  $(T_c - T)$ . This contrasts with the behavior of almost all the simpler previous theories where the difference is proportional to the square root of  $(T_c - T)$ .

Lee & Yang likewise calculated the pressure and fugacity of the two coexisting phases and of the mixture of critical density at any temperature. The complete expression for the fugacity as a function of composition, which corresponds to the magnetization curve as a function of applied field, has not yet been found, however.

Kaufman & Onsager (54) also obtained some of the functions for the correlations between the spins of neighboring lattice sites. These could be used to test the approximate results of the general theory of distribution functions discussed later.

As yet relatively little progress has been made with the matrix method applied to three-dimensional problems. Several steps have been taken in this direction by Montroll (76), Lassettre & Howe (61), Ashkin & Lamb (3), and Domb (21). Two-dimensional lattices with coordination numbers other than four have been treated by Wannier (109, 110) with the Onsager method.

*The "spherical" model.*—Another model whose consequences can be worked out exactly has recently been found by Montroll (77), Berlin, Kac & Thomsen (6, 7), and Lax (63). This consists of a lattice of dipoles with continuously variable orientation. Instead of holding the magnitude of each individual dipole constant, which leads to an intractable problem, the "sphericalization" procedure consists of holding the sum of the squares of all the dipoles constant. The thermodynamics of the model can be worked out even for the three-dimensional problem, assuming classical statistics. A single third-order transition with a flat, finite branch point in the heat capacity and dielectric susceptibility is found for the three-dimensional lattice, but no transition appears for one or two dimensions. Berlin & Kac (6) suggest that

the lack of a transition in two dimensions is related to the fact that the dipoles may orient continuously and isotropically as opposed to the two anisotropic orientations for the Ising molecules. Lewis & Wannier (67) have since found a simpler mathematical method of treating the model. It would be interesting to have a detailed comparison of these results with those of Oguchi & Takagi (86) discussed earlier.

#### STATISTICAL TREATMENTS APPROPRIATE TO ALLOYS

The first-approximation treatments are based upon several premises: (a) that the configurational partition function is separable from other partition functions, such as the vibrational; (b) the assumption of noninteraction of local pairs, i.e., that the relative probabilities for a pair of neighboring sites to be occupied in the several possible ways are independent of the manner of occupation of all other sites; (c) that the interaction between atoms that are not nearest neighbors can be neglected; (d) that the interchange energy,  $w$ , is independent of temperature, degree of order, and interatomic distance.

Recent treatments of the problem of order-disorder are directed at removing or weakening the effect of these various assumptions, and hence it will be convenient to discuss briefly the recent contributions from the point of view of their departure from the assumptional background of the first-order approximations. For the earlier elaborations of the theory the reader is referred to the excellent review by Nix & Shockley (83).

*Configurations of local groups.*—Although the degree of error introduced by the assumption of noninterference of pairs is difficult to evaluate, it is clear that the error will be larger for the case of a close-packed lattice than for a looser one. An obvious way of decreasing this error is to take groups of neighboring sites larger than pairs. Li (69) has extended the quasi-chemical theory in this manner while retaining all the other hypotheses and has taken as the local group a square, rhombus, tetrahedron, etc., for the quadratic, simple cubic, body-centered cubic (b.c.c.), and the face-centered cubic (f.c.c.) lattices. Li finds that the accuracy of the approximation increases as the ratio  $nz/(2p)$ , which characterizes the local group, decreases to unity; in this ratio  $z$  is the coordination number,  $n$  the number of sites in the chosen group, and  $p$  the number of nearest pairs per group. For the b.c.c. lattice, the calculations lead to a latent heat of zero for the transition from order to disorder even for the local group having the lowest value of  $nz/(2p)$  of those examined. Nevertheless, even the pair approximation is sufficient to lead to a superstructure, although the approximations characterized by smaller values of  $nz/(2p)$  lead to successively lower values of the critical temperature of ordering,  $T_c$ , and to larger values of  $\Delta C_v$ , the discontinuity of molar heat capacity through the transition. On the other hand, for the f.c.c. lattice, neither the pair nor the rhombus approximations leads to a stable superlattice, whether of the AB or the AB<sub>3</sub> type. Only when the tetrahedron is taken as the local group can the quasi-chemical approach account for the superstructure in the f.c.c. lattice, yielding as well a nonzero latent heat for the transition. It is interesting to

note that the pair and the rhombus do not include in themselves the characteristic feature of a f.c.c. lattice, namely, that there are nearest neighbors among the first-shell neighbors to any one site.

Guggenheim & McGlashan (39) similarly apply the quasi-chemical method to local groups of triangles and tetrahedra in the theory of regular solutions. McGlashan (70) has applied this development both to CuAu and to  $\text{Cu}_3\text{Au}$  with results (for the tetrahedron approximation) identical with those of Li (69). It should be noted that both Li and McGlashan ignore the tetragonality of the ordered CuAu.

Li (68) has formally extended the quasi-chemical method to consider  $m$  sublattices; the number of sublattices to be chosen for any specific application must be determined from experimental information. Li treats the Cu-

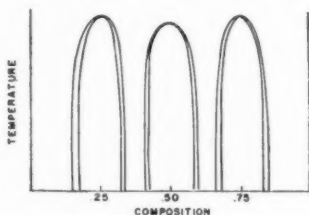


FIG. 1. Phase diagram for the Cu-Au system calculated by Li (68).

Au system in detail, using four simple-cubic sublattices and the tetrahedron as the local group, maintaining all the assumptions of the quasi-chemical theory. He calculates the phase diagram shown in Figure 1, showing three almost equal regions of order, each one separated from the disordered phase by regions of coexistence of ordered and disordered phases. In contrast with Shockley's (100) calculated phase diagram, the present work shows that the disordered state is stable at any temperature when the Cu-Au alloy contains a proportion of one species less than 17 per cent of the total; however, short-range order does persist in that range of composition. Furthermore, even as the temperature approaches zero, the coexistence of ordered and disordered phases is possible. The discovery of the existence of a superlattice at the  $\text{CuAu}_3$  composition (44) aptly confirms this ordered structure predicted by Li's calculations. It is worthwhile to point out that a theory in terms of four simple-cubic sublattices cannot bring out the existence of the orthorhombic superstructure reported by Johansson & Linde (49) for the Cu-Au system. This structure occurs at temperatures higher than the critical temperature of the tetragonal phase, and the orthorhombic phase differs from the tetragonal only by regular step shifts. Li asserts that his general theory could comprehend the orthorhombic phase by a suitable choice of local group and assignment of sublattices. Li also sketches the formal extension of the theory to more than two components.

*Interactions of more distant neighbors.*—Modification of theory to consider other than only nearest-neighbor interactions has been made by Sato (97, 98) using the zeroth-order (Bragg-Williams) approximation. The concept of the "order" of a superlattice is introduced and defined according to the effective range of interaction necessary to explain that superlattice. A "lower-order" superlattice will be stable at higher temperatures than will the "higher-order" superstructure. Interactions among other than nearest neighbors may be necessary to explain a superlattice with a large unit cell. It is pointed out that these ideas are not applicable to the orthorhombic superstructure in the Cu-Au system, and some aspects of Brillouin zone theory are suggested to explain it.

Matsuda (72) has treated the formation of the  $AB_3$  type of superstructure in the b.c.c. lattice considering interactions between next-nearest neighbors. Adachi (1) studied the influence of the next-nearest-neighbor interaction throughout the whole composition range in the b.c.c. lattice. Except for this elaboration, all the assumptions of the zeroth approximation were retained. For low values of the ratio of first-neighbor interchange energy to second-neighbor interchange energy, all transitions are of second-order, i.e., with zero latent heat, but as this ratio increases, some of the transitions become first-order. It is notable that this treatment allows the possibility of transformation, as the temperature is raised, from the  $AB_3$  type superstructure to the AB type, and then to the disordered phase. Coexistence of ordered and disordered phases is not considered.

However, the value of taking account of second-neighbor interactions within the framework of the zeroth approximation is placed in serious doubt by the work of Guggenheim & McGlashan (40) who treated the next-nearest-neighbor interaction from the point of view of the more accurate quasi-chemical method applied to quadruplets as the local groups. Assuming that the interaction energy between two molecules varies as the inverse sixth power of the distance between them, and focusing attention on the b.c.c. lattice in which the effect of next-nearest neighbors may be expected to be greatest, these authors show that the effect of taking into account the more distant neighbors is completely negligible in, for example, the calculation of the activity coefficient or of the heat of mixing.

Cowley (16) has carried through for  $Cu_3Au$  essentially the same kind of treatment as has Adachi (1) for more general cases, save that the relationship between the next-nearest-neighbor and the nearest-neighbor interaction energies is obtained from Cowley's experimental data (15) for  $Cu_3Au$ . This elaboration produces a nonzero latent heat for the transition in  $Cu_3Au$  and a sharp discontinuity in the order parameter.

*Variation of the interaction energy.*—Extension of the theory of order to consider variation of interchange energy with composition has been done by Cowley (16) for the Cu-Au system. Using the zeroth approximation with only nearest-neighbor interaction, he assumes that the interchange energy varies as the inverse sixth power of the unit cell dimension. The phase dia-



gram thereby calculated displays qualitatively the same lack of symmetry evinced by the experimental phase diagram, in that the critical temperature is highest for CuAu, lower for Cu<sub>3</sub>Au, and lowest for CuAu<sub>3</sub>.

Sato (96) incorporates an explicit dependence of interchange energy upon the degree of order and composition into the zeroth-order approximation. He writes

$$w = 1/2(V_{AA} + V_{BB} - 2V_{AB}) = V_0 e^{f(s, \theta)/a}$$

in which  $s$  is the degree of order,  $\theta$  the composition;  $a$  is an adjustable parameter, and  $w = \lim V_0$  as  $a$  approaches  $\infty$ . Sato takes  $f(s)$  as a Gaussian distribution whose center is at a stoichiometric composition. He finds that for the AB case as the parameter  $a$  decreases, the order parameter versus  $T/T_c$  goes from a smooth curve to one with a sharp discontinuity characteristic of a first-order transition; also as  $a$  decreases the solubility range of the ordered structure becomes narrower and the critical temperature rises until the resulting phase diagram becomes characteristic of a system containing an intermetallic compound. On this basis the author asserts that a superlattice and an intermetallic compound differ only in degree.

Guggenheim (38) has shown that it is not necessary to regard  $w$  as independent of temperature. It is in fact possible to regard  $2w$  as the free energy decrease of the whole system when an AA pair and a BB pair are converted into two AB pairs. Then all the formulae for the free energy of mixing, the chemical potentials, or the activity coefficients remain unchanged by removing the restriction that  $w$  should be independent of temperature. However, the formulae containing heat functions are changed to the extent of replacing  $w$  by  $w - T(dw/dT)$ .

*Nonseparability of the configurational partition function.*—The interrelation between two simultaneous cooperative phenomena, the formation of a superlattice and the onset of ferromagnetism (and of antiferromagnetism), has been considered by Sato (95) on the basis of the Bragg-Williams approximation. The energy is calculated by assigning the usual chemical interaction energies and also magnetic interaction energies,  $J_{ij}$ ; the latter are assumed independent of local configuration, but the magnetic exchange energy is taken as an explicit function of degree of order and of composition. Sato finds that if  $J_{AA} + J_{BB} - 2J_{AB} > 0$ , the magnetic Curie temperature decreases as the degree of order increases, as is found for Fe<sub>3</sub>Al; if  $J_{AA} + J_{BB} - 2J_{AB} = 0$ , the formation of the superlattice and the onset of ferromagnetism occur quite independently, as appears to be the case in FeCo. Only in such a case can the magnetic energy be distinguished experimentally from the configurational energy. However, if  $J_{AA} + J_{BB} - 2J_{AB} < 0$ , the magnetic Curie point rises as the degree of order increases, as appears in Ni<sub>3</sub>Mn.

*Experimental studies of order-disorder phenomena.*—We shall briefly outline the recent experimental contributions which shed some light on the suitability and applicability of the various statistical treatments already de-

scribed. For earlier references the reader is again directed to the review by Nix & Shockley.

Walker (108) followed the variation with temperature of the long-range order in the alloy CuPt by measuring the intensity of superstructure x-ray diffraction lines of specimens quenched from various annealing temperatures. He found that the long-range order parameter decreases slowly with increasing temperature to 0.77 at the critical temperature of 815°C., whereupon there is an abrupt drop leaving only short-range order at higher temperatures. The ordered structure can be regarded as a segregation of Cu and Pt atoms on alternate (111) planes, so that each atom has the same number of unlike nearest neighbors below and above the transition. Because of this fact, Walker points out that any theory based on the concept of spherically symmetrical nearest-neighbor interactions is bound to fail when applied to this alloy and suggests the possibility of considering directional ordering forces.

The long-range order parameter in  $\text{Cu}_3\text{Au}$  varies with temperature in a fashion very similar to that in CuPt. The alloy  $\text{Cu}_3\text{Au}$  was studied by Cowley (15) by x-ray diffraction from a single crystal held at the elevated temperatures, so that the possibility of artifacts arising during quenching is obviated. The short-range order parameters were also measured from the diffuse background scattering of x-rays from the crystal held at temperatures above the critical. Oriani (88) showed that the nearest-neighbor distribution obtained from thermodynamic data (112) agrees reasonably well with Cowley's data.

Roberts (93) finds the same sharp drop of long-range order parameter at the critical temperature for the alloy CuAu. In contrast, Chipman & Warren's results (14) by x-ray diffraction from a single crystal of  $\beta$ -brass ( $\text{CuZn}$ ) held at elevated temperatures show that the long-range order parameter decreases continuously with increasing temperature; no discontinuity is apparent. Interestingly enough, Muldawer (78) has found that  $\beta$ -AgZn, which like  $\beta$ -brass has the b.c.c. lattice above the  $T_c$ , shows a behavior intermediate between that characteristic of  $\beta$ -brass and that of CuAu. However, the possibility exists that the ambiguity is at least partially caused by the necessity of adding a small amount of gold to the AgZn alloy in order to suppress another structure which would otherwise form during slow cooling.

The behavior described above for  $\text{Cu}_3\text{Au}$  and for  $\beta$ -brass was confirmed by Keating & Warren (55) by x-ray diffraction from single crystals held at elevated temperatures. The purpose of this work was to decide whether in each of these alloys below the critical temperature there is a single ordered phase whose order changes with temperature, or whether there coexist an ordered and a disordered phase, the relative amounts of which vary with temperature. The experiments clearly decide in favor of the single ordered phase for these two alloys near the stoichiometric compositions. Because the sample temperature was uncertain by about  $\pm 5^\circ\text{C}$ ., the results do not exclude the existence of a very narrow two-phase region in  $\beta$ -brass near the critical temperature. Furthermore, for  $\text{Cu}_3\text{Au}$ , though a narrow two-phase

region is not expected at the critical temperature of the stoichiometric composition, the measurements clearly do not exclude the possibility of two-phase regions at compositions removed from the stoichiometric.

The equilibrium coexistence of an ordered and a disordered phase has been established by Newkirk *et al.* (82) for nonstoichiometric alloys in the cobalt-platinum binary system. X-ray diffraction and microstructural investigation agree in fixing the two-phase regions at compositions around the CoPt alloy. Similarly, Edwards, Wallace & Craig (22) find equilibrium coexistence of an ordered and a disordered phase in Mg-Cd alloys of from 75 to 84 atom per cent Cd. Recent very careful x-ray diffraction work by Newkirk (81) on copper-gold alloys near the CuAu composition fixes the range of coexistence of ordered and disordered phases.

X-ray diffraction studies by Norman & Warren (84) on two compositions in the silver-gold system AgAu and Ag<sub>3</sub>Au, show that despite the absence of superlattices and despite the thermodynamically ideal appearance of the solidus and liquidus lines of the phase diagram, there is appreciable short-range order. Another, and a more striking disparity between what would be predicted from the phase diagram and what is actually observed is the case of alloys of Ni-Au studied by Flinn & Averbach (23). Their x-ray studies indicate a considerable degree of short-range order in the solid solutions adjoining the wide miscibility gap in this system, although the thermodynamic measurements on the same system by Seigel, Cohen & Averbach (99) indicate a large positive heat of mixing, and an entropy of mixing much larger than the ideal. The anomalous sign of the heat of mixing is attributed to lattice deformation energy, and the larger-than-ideal entropy of solution is attributed to a contribution from the change in lattice vibrations owing to the solution process.

Other studies that show that caution must be exercised in deducing local atomic configuration from thermodynamic measurements include the thermodynamic data of Weibke & Matthes (111) on Cu-Pt alloys, which yield a larger-than-ideal entropy of mixing and an activity coefficient for Pt larger than unity; the thermodynamic data of Oriani (89) likewise yield a larger-than-ideal entropy of mixing and an activity coefficient for Pt larger than unity, but also a heat of solution that is a positive quantity; the thermodynamic data of Trumbore, Wallace & Craig (103) for the Cd-rich alloys of Mg-Cd yield a larger-than-ideal entropy of mixing, which the authors attribute to the existence of lattice vacancies. In all these cases, the deviations from the predictions of any of the modifications of the quasi-chemical theory must be attributed to other factors beyond the configurational. These factors, though influencing the thermodynamic measurements, are necessarily not considered in the configurational theories. On the other hand, the thermodynamic data on Cd-Ag alloys and Ag-Zn alloys by Birchenall & Cheng (9), and the data on Ag-Zn alloys by Underwood & Averbach (106) yield reasonable values of short-range order when the quasi-chemical theory is applied to them.

## THE LIQUID-GAS CRITICAL PHENOMENON

*Point, line, or plane?*—The simpler lattice theories discussed above all have an ordinary critical point at which the two-phase region disappears with increasing temperature. In this respect they resemble the van der Waals and related theories of imperfect gases. In fact there is an underlying formal identity between the pressure of a one-component gas or liquid and the osmotic pressure of one of the components of a solution. This has been found a number of times, for example by McMillan & Mayer (71) in their theory of solutions.

Mayer (74, 75) was the first to challenge the concept of a simple critical point. He showed that the series for the pressure of a gas in terms of its density, the usual virial series, would diverge at the condensation density. The critical point, however, is the first point at which the derivative of the series vanishes as the temperature is lowered. There is no obvious connection between the point of divergence of a power series and the point at which its derivative is zero. Therefore it may be argued that an interval between the critical temperature and the point of condensation would be likely. Mayer discussed the properties that a fluid in this interval ("derby hat region") would have, if it existed. He suggested that there would be a planar region in the  $p, V, T$ , diagram within which  $p$  was independent of  $V$  but which would not be a two-phase region.

On the other hand, Rice (92) has advanced arguments tending to show that there should be no temperature interval between the point of zero slope and the two-phase region but that there should be a range of densities at one temperature where the rate of change of  $p$  would be zero. In other words, he proposes that the critical point should actually be a horizontal critical line in the  $p, V, T$ , diagram, and that the coexistence curve should have a straight segment at the top.

The experimental evidence for and against these hypotheses has been discussed in a review by Hildebrand & Scott (42, 43). Since that time a further study has been made by Wentorf (113) on carbon dioxide and sulfur hexafluoride. The experimental results in general seem to favor a critical point rather than a line or plane, but there are so many anomalous effects in the critical region that the evidence is hardly conclusive.

We have seen that the predictions of the approximate theories for the heat capacity and for the shape of the coexistence curve in the neighborhood of the critical point are unreliable. There is no reason to think that they are more reliable in regard to the shape of the critical region. The exact theory of the two-dimensional Ising lattice, however, does rule out the Mayer and the Rice possibilities for this particular system, giving instead a single critical point and a rounded coexistence curve. Nevertheless it is noteworthy that the coexistence curve is much flatter than the parabola given by the approximate theories, so that it really stands intermediate between the older ideas and those of Mayer and Rice.

The Mayer theory should apply just as well to the two-dimensional Ising

lattice as to any three-dimensional system. The problem therefore arises as to what is the connection between the divergence and the vanishing of the derivative of the virial series on which Mayer based his hypothesis. Zimm (117) has recently shown that a certain approximation of Kirkwood's, the superposition approximation discussed below, leads to the result that the critical point is a singularity at which not only the first derivative of pressure with respect to volume, but also all higher derivatives vanish. If the critical point is itself a singularity it could be understood how it would be associated with the onset of the divergence of the virial series. Unfortunately, however, Zimm also showed that Kirkwood's superposition approximation is inconsistent with the existence of a point of inflection at the critical point so that its consequences cannot be relied on. Experimental isotherms, however, are much flatter than the cubic curves of the simple theories in the neighborhood of the critical point in accord with Zimm's result. In any case the true state of affairs seems likely to be here also intermediate between the classical theories and Mayer's hypothesis.

Some discussion of the mathematical details of Mayer's theory has occurred recently. Yang & Lee (115) and Katsura & Fujita (52) independently have pointed out that in the Kahn & Uhlenbeck (51) formulation of Mayer's theory, which has been accepted by later authors, the limit of infinite volume was approached incorrectly. The correct method of approach apparently does not change any of the conclusions concerning condensation, but it does permit the condensed phase to be included formally in the theory in a more satisfactory way.

*The integral equation theories.*—Noteworthy effort has recently gone into the program of developing theories of fluids not dependent on a lattice model. Prominent in this effort have been the integral equation methods introduced by Kirkwood (59) and Yvon (116), and more recently extended by Mayer (73), Born & Green (11), and numerous other contributors. The discussion makes use of the molecular distribution functions  $n_1(i)$ ,  $n_2(i,j)$ ,  $n_3(i,j,k)$  which give the density per unit volume of single molecules, pairs, and triplets respectively. The integral equations relate derivatives of  $n_2(i,j)$  to integrals of  $n_3(i,j,k)$ . To solve the equations the approximation is made that  $n_3(i,j,k)$  can be written as a product of the functions  $n_2$  of the three pairs of molecules  $i,j,k$ . This is the superposition approximation referred to above. The result is a nonlinear integral equation for the pair distribution function. The equation has a singularity at a certain value of the density at which the fluctuation quantity  $n_2(i,j) - n_1(i)n_1(j)$  becomes nonintegrable. Born & Green interpret this point as the density dividing the liquid from the vapor, since it is the first singular point to appear as the density is raised. The numerical calculations of Rodriguez (94) on the equation of state of argon are in accord with this interpretation. Kirkwood, (101A), on the other hand, regards it as the point at which crystalline order appears in the fluid phase, and hence as more analogous to a melting point. The fact that the singularity appears even in a fluid of nonattracting hard spheres certainly supports this view. Further work is clearly needed.

Green has recently published a book on the theory of liquids which gives an up-to-date discussion of this and related topics (36) [see also a recent article by de Boer (10)].

#### PHASE TRANSITIONS ASSOCIATED WITH ROTATIONAL DISORDERING OF MOLECULES IN CRYSTALS

*Introduction.*—The specific heat curves of a number of molecular and ionic crystals composed of highly symmetrical particles show anomalies which resemble those observed during order-disorder transitions in alloys. Other properties, such as the proton resonance line-width and dielectric constant frequently show discontinuities at the same temperature at which the specific heat anomaly appears. Such phenomena suggest that certain molecules or ions in the solid state undergo some kind of rotation which is connected with the appearance of a phase transition.

Our first concern will be the two different hypotheses regarding the general nature of molecular rotation in solids, namely, those of Pauling and Fowler, and Frenkel.

*The free rotation hypothesis of Pauling; Fowler's extension with cooperative effect.*—Pauling suggested that below a transition temperature certain molecules in the solid state oscillate about equilibrium positions in a potential which was taken as sinusoidal for convenience, but above this temperature rotate freely (90). This simple hypothesis is able to account for a rise in dielectric constant and a drop in specific heat at the transition temperature. A change from oscillation to free rotation will cause the specific heat at constant volume,  $C_v$ , to drop  $R/2$  units per degree of freedom of rotation as the temperature is raised through the transition. This drop of  $C_v$  at the transition is a result of the fact that rotators in classical theory have only half as large a specific heat per degree of freedom as oscillators.

Fowler (24) extended Pauling's concept of free rotation by explicitly introducing the idea that molecular rotation in solids is a cooperative phenomenon. Fowler assumed that polar diatomic molecules in a molecular crystal are constrained by a sinusoidal potential of magnitude  $W$ , and further assumed that a given molecule could surmount this restricting potential and rotate if it had sufficient kinetic energy to turn an arbitrary fraction,  $\beta$ , of  $180^\circ$  from its equilibrium orientation. Fowler then calculated the fraction  $S$  of molecules "not rotating," and  $C_v$  as a function of reduced temperature with the help of the Bragg-Williams approximation,  $W = W_0 S$ , and obtained first or second-order transitions<sup>2</sup> according to the value of the arbitrary

<sup>2</sup> Fowler calculated the dielectric properties for this model using the internal field of Lorentz. This led to two discontinuities in the dielectric constant. One of these was the rotational transition at  $T_c$ , while the other was a result of the  $4\pi/3$  catastrophe. The more recent calculations of Kirkwood, who assumed a potential similar to that used by Fowler, suggest that the latter type of "transition" will not appear in systems consisting of rotating dipoles (58).

parameter  $\beta$ . The transition, which occurs at  $T_c = \beta W_0/k$ , marks the onset of completely free rotation, i.e.,  $S = W = 0$  above  $T_c$ .

Fowler's theory leads to a drop of  $C_v$  at  $T_c$  of up to  $4R$  depending on the value of  $\beta$ . We mention this because a drop of  $R/2$  units per degree of rotational freedom is sometimes used as a criterion for free rotation following the original hypothesis of Pauling, but Fowler's calculations prove that the drop of  $C_v$  at the transition will exceed this in cooperative systems. A common feature of the theories of Pauling and Fowler is that the rotation is assumed to be free above the transition.

In passing, it is worth mentioning that Fowler's theory reduces to

$$S = \tanh(W/2kT), \quad W = W_0 S \quad 1.$$

for the case  $\beta = \frac{1}{2}$ . This is analogous to the result obtained by Bragg & Williams for binary alloys; the fraction of molecules "not rotating" is equivalent to the long-range order parameter. Kirkwood has removed a number of arbitrary features from Fowler's theory (58).

*Frenkel's concept of orientational order.*—Frenkel believed that the rotation of molecules above the transition was not at all free but consisted of rotational oscillations about more or less randomly distributed equilibrium positions (27, 28). Like Pauling and Fowler, he considered that the molecules were subject to a potential barrier below the transition. In Frenkel's view, the transition point is the temperature at which there is a loss of long-range order in the orientations of the molecules, with respect to both each other and the crystal axes. In extreme cases all that remains above the transition is a limited degree of local order.

It is desirable to distinguish the order-disorder process in alloys from the disordering process envisioned by Frenkel. In the former, certain atoms move to sites in the superlattice formerly occupied by other atoms, while in the latter the molecules remain on the lattice sites but rotate about their centers of gravity to new equilibrium orientations. The process described by Frenkel is, therefore, called "rotational" or "orientational" disordering.

One consequence of Frenkel's hypothesis (ignoring cooperative effects for the time being) is that  $C_v$  will not drop at the transition since the "rotation" is assumed to be essentially vibrational in character both above and below the transition. Actually, rotational disordering is co-operative in nature, so we should expect the usual rise of  $C_v$  below the transition with a concomitant drop above, just as in the co-operative free-rotation case. Thus, the drop of  $C_v$  at the transition is in itself not a reliable criterion for free or hindered rotation. Fortunately, Lawson's method of dealing with  $C_v$  (next section) and methods for other physical properties are capable of distinguishing between free and hindered rotation in crystals. Frenkel's concept that rotation is hindered above the transition does not preclude the possibility that the dielectric constant of the phase above the transition will be high (see below).



We turn now to a discussion of present knowledge of the transitions in some of the substances originally discussed by Pauling (90).

*The ammonium chloride  $\lambda$ -transition.*—In a careful study, Lawson (62) measured the specific heat at constant pressure,  $C_p$ , for ammonium chloride in the vicinity of the  $\lambda$ -transition at 242.8°K., and from these and his thermal expansion and compressibility data, computed values of  $C_v$ . We note that the value of  $C_v$  computed by Lawson is not the heat capacity at a particular constant volume, but at a series of volumes corresponding to a series of temperatures. The difference between  $C_p$  and  $C_v$  is extremely large in the transition region, and this emphasizes that care must be taken to compare theory, which yields the configurational specific heat, with the appropriate experimental data.

Lawson shows rather conclusively that the  $\text{NH}_4^+$  ion does not rotate freely above this transition although the drop in  $C_v$  of about  $3R/2$  is in accord with Pauling's simple free-rotation picture. Lawson deals only with the value of  $C_v$  above the transition where co-operative contributions to  $C_v$  are not large. The experimental value of  $C_v$  above the transition is  $9R$ ;  $6R$  of this value is attributable to the normal vibrations of the ammonium chloride lattice. The free rotation theory suggests that the  $\text{NH}_4^+$  tetrahedra will contribute an additional  $3R/2$  to  $C_v$ , while the rotational oscillation hypothesis of Frenkel indicates that the tetrahedra should contribute an additional  $3R$  to  $C_v$ . Clearly, only the Frenkel hypothesis permits a full accounting of the actual value of  $C_v$  above the transition.

Further evidence that the  $\text{NH}_4^+$  ions do not rotate freely above the transition is afforded by the infrared measurements of Wagner & Hornig (107) which show no rotational fine structure in the room temperature form of ammonium chloride. These authors favor the view that the  $\text{NH}_4^+$  tetrahedra are randomly distributed between two possible orientations above the transition. They criticized, on the grounds of impurity, the work of an earlier investigator who found evidence for free rotation. Similarly, the proton resonance experiments of Gutowsky & Pake (41) suggest tunneling or hindered rotation, but not free rotation.

The orientation of the protons (or deuterons in  $\text{ND}_4\text{Cl}$ ) of both the low and high-temperature forms of ammonium chloride has been examined by Goldschmidt & Hurst (33) using neutron diffraction techniques. Levy & Peterson (65) have repeated the work of these authors on the room-temperature form, and obtained different results. This discrepancy has fortunately been eliminated, since Goldschmidt & Hurst's latest measurements (34) are now in agreement with those of Levy & Peterson. The structures found by the above authors are illustrated in Figure 2. The neutron diffraction results show decisively that the ammonium chloride transition involves orientational disordering of the ammonium ions of the general type proposed by Frenkel.

Other ammonium halides will not be discussed here in detail since much



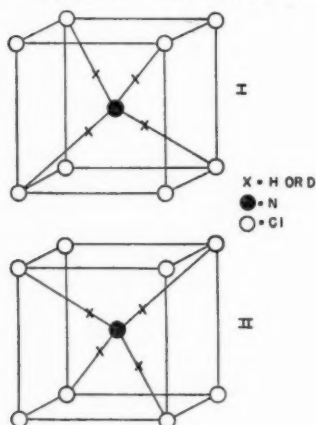


FIG. 2. The two orientations of the ammonium ion above the  $\lambda$ -transition in ammonium chloride according to Levy & Peterson. Only one of the two orientations is occupied below the  $\lambda$ -transition.

important work is now in progress. It is worth mentioning, however, that Stephenson, Landers & Cole (102) have suggested on the basis of specific heat data that the  $\text{NH}_4^+$  ion in ammonium iodide may be rotating freely above the highest transition point. The recent neutron diffraction studies of Levy & Peterson (66) appear to eliminate the possibility of three-dimensional free rotation of the  $\text{NH}_4^+$  ion for both ammonium bromide and iodide, but single-axis free rotation is not excluded.

Nagayima (80) anticipated the correct molecular picture of disordering at the  $\lambda$ -transition in ammonium chloride prior to the neutron diffraction and infrared spectra studies. Nagayima calls the two possible orientations of the  $\text{NH}_4^+$  ion I and II (Fig. 2), and sets the probability that a given ion is in configuration I or II equal to  $p$  and  $1-p$  respectively. Using a treatment patterned after that of Bragg & Williams he then shows that

$$\tanh \frac{W(2p-1)}{kT} = 2p-1 \quad 2.$$

which is identical in form to the familiar Bragg-Williams expression derived for binary alloys. The quantity  $2p-1$  is equivalent to the long-range order parameter of Bragg & Williams. As one would expect for a two-position theory, equation 2 yields a second-order transition at  $T_c = W/2k$ , where  $p$  becomes  $\frac{1}{2}$  (random occurrence of I and II in the lattice). The calculated drop of the configurational heat capacity at  $T_c$  is in surprisingly good agreement with the data on  $C_v$  as calculated by Lawson (62). (See however re-

mark regarding  $C_p$  above.) The basal specific heat does not drop an extra  $3R/2$  at  $T_c$  as suggested by Fowler's free-rotation theory, since the motion of the tetrahedra is essentially vibrational in character above and below the transition. Nagayima's paper should be consulted for other important calculations.

*Long-chain compounds.*—Long-chain hydrocarbons and their polar derivatives frequently exhibit solid-state transitions just below the freezing point if they contain 22 or more carbon atoms. There are good reasons to believe that these transitions involve rotation of the rod-like molecules about the long axis. For example, Müller (79) showed that long-chain hydrocarbons exhibit the packing of cylinders above the transition, and ascribed this to some type of rotation about the long molecular axis. Similarly, the dielectric measurements of various workers also revealed transitions, and suggested single-axis rotation (5, 17, 18, 45, 46) above the transition. Finally, the recent proton resonance experiments of Andrew (2) confirmed the rotation of certain long-chain hydrocarbon and alcohol molecules about the long axis. Furthermore, there are reasons for supposing that the rotation of the molecules is hindered above the transition. Foremost among these is the fact that the dielectric relaxation time observed for some long-chain esters (18) and bromides (46) above the solid-state transition temperature is considerably longer than one would expect on the basis of free rotation. Andrew, however, has suggested that a large fraction of the molecules in long-chain hydrocarbons may be rotating freely above the transition (2). Despite this view, the Frenkel viewpoint of hindered rotation has been adopted in the theories discussed below. We shall return to this point.

Fröhlich has outlined a theory of single-axis rotation, which he applies to long-chain ketones (29, 32). He assumes that by turning about the long axis, polar long-chain molecules are capable of assuming either of two mutually opposed positions which differ by a potential energy  $V$ . The more stable of these positions is called the "right" position, and the less stable the "wrong" position. Using  $w$  to denote the probability that a molecule is in the "wrong" position and  $1-w$  the position is "right," he finds

$$1 - w = 1/[1 + \exp(-V/kT)] \quad 3.$$

The quantity  $1-2w$  is a measure of the long-range orientational order. Fröhlich, following the concepts of order-disorder theory, now considers that  $V$  will be a function of temperature going to zero at a transition temperature; the result is that a plot of  $1-2w$  against  $T$  bears a strong resemblance to the plot of order versus  $T$  given by Bragg-Williams theory. This two-position theory inevitably leads to a second-order thermal transition in accord with the experiments of Ubbelohde (see below). Fröhlich then shows that the polarizability is given by

$$\alpha = \frac{\mu^2 4w(1-w)}{3kT} \quad 4.$$

Using his generalized dielectric theory, Fröhlich further shows that the dielectric constant will show a broad cusp-like peak at the transition<sup>3</sup> (Fig. 3). Above the transition,  $w = \frac{1}{2}$ , and the polarizability becomes  $\mu^2/3kT$ , the classical "free-rotation" value; a potential barrier still separates the two available positions which are now equivalent. In applying the theory to ketones (which have no transitions) Fröhlich assumed the transition was at or above the melting point (29). Crowe, Hoffman & Smyth have suggested reasons for the failure of transitions to occur in ketones (17). In commenting on the entropy of transition predicted by two-position theory, which is  $R \ln 2$ , Fröhlich noted that the observed entropy of transition is much greater than this, and ascribed the additional contribution to severe internal twisting of the hydrocarbon chains in the solid state (31).

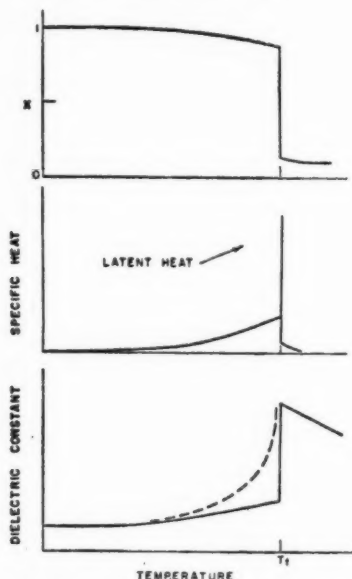


FIG. 3. The degree of rotational order,  $x$ , specific heat and dielectric constant as a function of temperature according to the many-position model of single-axis rotation in long-chain compounds (solid lines). Dashed line in lower curve shows dielectric behavior calculated using two-position model.

The belief that the transition and melting points of pure long-chain compounds are second-order or "lambda" transitions is a result principally of the measurements of Ubbelohde (104). Ubbelohde's data indicate that

<sup>3</sup> Simpson (101) has shown that the peak in the dielectric constant will not appear in the two-position case for certain types of interaction.

the melting and transition points of certain long-chain hydrocarbons are characterized by broad, cusp-like peaks in the specific heat rather than isothermal latent heats. Ubbelohde called this phenomenon "monophase premelting" (105) in the belief that it was a property of extremely pure materials; Fröhlich proposed that this effect was a result of chain-twisting (30, 31). The concept that the melting and rotational transition points in pure long-chain compounds are unsharp is not universally accepted. For example, the thermal data of Hoffman & Decker (47) on carefully purified hydrocarbons show unmistakable isothermal latent heats at the transition points, and these authors attribute to impurities the greater part of the "monophase premelting" observed by Ubbelohde. It is also worth pointing out that the dielectric constant of polar long-chain molecules does not generally follow Fröhlich's calculated curve shown in Figure 3. Instead, the dielectric constant of purified materials rises abruptly to a liquid-like value at the transition or melting point as shown by the recent work of Crowe & Smyth (18), Daniel & Stark (20), and others (5, 45, 46). The dielectric data provide convincing evidence that rotational transitions and melting points in a significant number of long-chain compounds are first-order. A few small lambda transitions have been observed in polar compounds by thermal methods, but the change in dielectric constant associated with them is virtually nil; exceptions are possible, however.

Since a two-position theory (or a chain-twisting theory) cannot ordinarily lead to first-order thermal and dielectric transitions, Hoffman (46) was led to advance a "many-position" theory based on a scheme proposed by Frank (26). This produced the observed type of transition and explained without the assumption of severe chain-twisting the anomalous entropy first noticed by Fröhlich.

In constructing the "many-position" theory (46), it was assumed (a) that long-chain molecules behave, to the first approximation, as rigid rods, (b) that each molecule has at low temperatures one stable rotational position (called "1"), (c) that  $\Omega$  equivalent positions (called "2") of potential energy  $V$  above the ground state become accessible as the temperature is raised. A constant barrier,  $W_0$ , is assumed present even when  $V$  is zero. It was anticipated from molecular models that  $\Omega$  would be at least eight. This potential energy picture is merely an obvious extension of that originally proposed by Müller (79). The fraction of molecules occupying the ground state,  $x = n_1/(n_1 + n_2)$ , was found to be

$$x = 1/[1 + \Omega \exp(-V_0 x/kT)] \quad 5.$$

with the help of the Bragg-Williams approximation,  $V = V_0 x$ , and the Boltzmann law,  $n_2/n_1 = \Omega \exp(-V/kT)$ .  $x$  is a measure of the long-range rotational order in this theory. Molecules in any of the  $\Omega$  rotational positions in state "2" are considered to be rotationally disordered. A discontinuous transition with a latent heat appears at a temperature

$$T_i = V_0/2k \ln \Omega, \quad 6.$$

as may be seen in Figure 3, where some of the properties calculated for the case  $\Omega = 12$  are shown. The "many-position" theory predicts a small rise of  $C_p$  which culminates in a latent heat. Similarly, the dielectric constant is characterized by a slow increase resulting from gradual rotational disordering which begins well below  $T_i$  and ends in an abrupt rise at  $T_i$  to a value near that of the liquid.<sup>4</sup> These results are in accord with the experiments mentioned previously.

Additional evidence that the rotation is not free above the transition was inferred from the entropy of transition (at constant volume) which is about  $R \ln 12$ . This value is well below that which one would expect on the basis of free rotation, and indicated that there are about 12 rotational positions in the disordered state. The value of  $\Omega$  was ascribed to the complicated shape of the untwisted molecule as viewed end-wise. Arguments based on the constancy with chain length of the entropy of transition, the linearity of a plot of transition temperature with chain length, and dielectric relaxation data were used by Hoffman & Decker to show that the twisting of hydrocarbon chains in the solid state was probably not severe (47).

*The hydrogen halides.*—Powles has given an illuminating discussion of the phase transitions in the solid hydrogen halides (91). The paper contains a compact summary of pertinent calorimetric, dielectric, and structural data.

The dielectric constant of the hydrogen halides as a function of temperature is shown schematically in Figure 4 to display the succession of phases. All the transitions are second-order except those in HCl and DCl.

Powles has shown that the broad III-II transition in HBr and HI is not controlled solely by dipolar forces by comparing  $\mu^2/r_0^3$  and  $kT_1$ , where  $r_0$  is the intermolecular separation and  $T_1$  the transition temperature. The parallelism is, in fact, so poor as to suggest that dipolar forces play only a minor role. A different view on the controlling feature of the III-II transition has been expressed by Tisza (101a). Powles then went on to show that the second-order II-I transition is controlled almost completely by dispersion forces.

The entropies of transition of HCl, DCl, HBr, DBr, HI, and DI were found next using  $\Delta S = R \ln n$ . Powles found that the sum of the entropies of transition for each of these compounds was about  $R \ln 4.5$ . HBr was anomalous in this respect, and gave  $\Delta S = R \ln 3.2$ . Since the molecules are known to be orientationally fixed in phase III, Powles inferred that each molecule occupies approximately four rotational "sites" in phase I. Thus, the rotation of the molecules is not at all free even in the high temperature solid form of the hydrogen halides. A simplified view of the structure of phase I, which is body-centered cubic, suggests that the molecules may occupy any of six

<sup>4</sup> The potential becomes nearly symmetrical above  $T_i$ . The polarizability of a dipole in a symmetrical sinusoidal potential well with three or more minima of any depth is  $\mu^2/3kT$ , the classical "free-rotation" value. Such a model thus leads to liquid-like values of the dielectric constant, but the dielectric relaxation-time will be longer than the free rotation value.

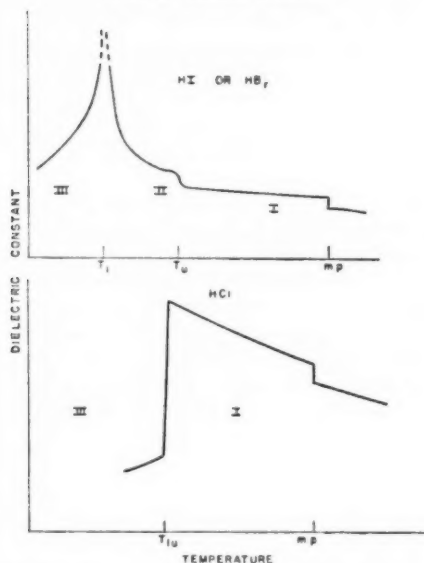


FIG. 4. The dielectric behavior of the hydrogen halides in the vicinity of the solid-state transitions (schematic). An additional small anomaly (not shown) appears near  $T_{II}$  in HBr, but not in DBr.

alternative positions so that  $\Delta S$  would have a maximum value of  $R \ln 6$ . Powles ascribed the difference between the experimental values of  $n$  and the value of  $n=6$  to protuberances on the molecules which block certain configurations.

The entropy of the broad III-II transition is about  $R \ln 2$ . This implies that a two-position orientational order theory, which will naturally lead to second-order transitions, may be applicable in this case. The plausibility of the two-position model is strengthened by the fact that the two-position dielectric theory of Fröhlich (29, 32) leads to a qualitatively correct type of behavior of the dielectric constant at the III-II transition. The recent dielectric measurements of Brown & Cole (13) indicate that the peak in the dielectric constant at the III-II transition in HBr is much higher than that found by Powles or computed theoretically by Kirkwood (58). It may prove very difficult to obtain a fairly exact theory of the dielectric constant near the low-temperature transitions in HI and HBr. However, we should note that the specific heat associated with the III-II transition in HBr bears a resemblance to that calculated by Onsager in his exact treatment of the two-dimensional Ising lattice.

*Comment on theoretical calculations.*—So far we have mentioned only theoretical calculations which were appropriate to specific transitions selected principally for the availability of relevant experimental data. Because of the complexity of real substances, some of the theories have been highly approximate, although not necessarily misleading. We now consider briefly the status of more refined calculations with regard to their applicability to real substances.

The refined rotational transition theory of Oguchi (85), Oguchi & Takagi (96) and the calculations on the "spherical" model (6, 7, 63) of dipoles on a lattice yield second- or third-order transitions. While a few such are known to occur, as the III-II transition in the hydrogen halides, a large number of rotational transitions are first-order. This is particularly the case with the nearly spherical organic molecules (e.g., 2,2-dinitropropane) studied by Smyth and co-workers (4, 19). This probably means that more than dipolar forces are involved in these transitions. A theoretical study of the first-order transitions of nearly spherical organic molecules may prove rewarding.

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# EXPERIMENTAL MOLECULAR STRUCTURES<sup>1</sup>

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## INTRODUCTION

The most direct method for the determination of interatomic distances in individual molecules or molecular aggregates is the one which utilizes the diffraction of radiation of wavelengths comparable to molecular dimensions. For sufficiently simple molecules moments of inertia as determined by spectroscopic technics (in particular, the absorption of microwave radiation) may be combined for isotopically substituted variants, to give very precise values for distances and bond angles. The precision of such determinations is an order of magnitude greater than that based on the best diffraction technics.

Structural information of a qualitative nature may be derived from a large variety of physical measurements. The presence or absence of a center of inversion, or of a plane of reflection in a molecule is directly determinable from dielectric constant data, or the rotation of the plane of polarized light, respectively. The point group symmetry of a molecule is determinable by the mere counting of present, superposable, and absent fundamental vibrational frequencies in the infrared absorption and Raman spectra. The absence or presence of characteristic functional groups in a compound often may be ascertained, essentially on an empirical basis, by comparing its absorption spectrum with that of model compounds containing the groups in question. A host of molecular constants for which additivity relations have been proposed have been used extensively to establish the connexity between atoms in molecules. Finally, the moments of inertia may be roughly checked and the symmetry number deduced from a comparison of the third law entropy with that computed for the assumed molecular structure. Although it would be worthwhile to attempt a general review of experimental methods for structure determinations, we cannot give such an undertaking sufficient time to do it justice. Most significant would be a critical comparison of the information which is directly derivable from each technic. It is obvious, however, that the conclusions derived from different methods are complementary, so that it is worthwhile to investigate the structures of some molecules by several procedures. In case of the hexafluorides of uranium, tungsten, and molybdenum these complementary studies led to conclusions which were not mutually consistent. Dissatisfaction with such a state of affairs led to a significant discovery, the inadequacy of the first Born approximation. The complementarity of electron diffraction and microwave absorption data has been demonstrated many times. By combining these data results were obtained

<sup>1</sup> The survey of the literature pertaining to this review was concluded in January, 1953.

which are more reliable than those which could be deduced from either set by itself. Recent examples are the structures of perfluorobutylene-2 and trifluoro-methyl acetylene (data summarized below).

With regard to the three types of radiation available for diffraction investigations of molecular structure, a brief summary of their relative advantages and limitations is in place. Electron waves differ appreciably from neutron waves and x-rays in two essential respects, in wavelength and in scattering cross section. Whereas the wavelengths for neutrons and x-rays employed range from about 0.7 Å to about 2.5 Å, those for electrons range from 0.05 Å to 0.07 Å. As a consequence, the range in the diffraction variable [ $s = (4\pi/\lambda) \sin \theta/2$ ] which is generally covered for electrons is 1 to 30; in contrast, for x-rays and neutrons the range is 0.5 to about 8.5 with occasional data being extended to about 15. Thus, for diffraction by gases, liquids, or powders, considerably more data are obtainable with electron beams. One may get a feeling for the relative magnitudes of their scattering cross sections by comparing the atom form factors for the three types of radiation at  $s = 6.3$ .

$10^{12}F_{Na}$	1.14 (x-r)	0.34 (n)	6,700 (e)
$10^{12}F_{Cu}$	3.75 (x-r)	0.76 (n)	15,100 (e)

Clearly, because of their higher scattering cross section electrons are best suited for the study of gases or other low density phases. By the same token, the troublesome problems of absorption and multiple scattering become significant. The requirement of a good vacuum and very thin samples preclude the extensive use of electron beams for the study of single crystals. However, much more data, and consequently molecular structures which are freer of ambiguities, are derivable from diffraction studies of single crystals. In our opinion, the most encouraging recent development in this field has been the continued success of Lipscomb (1), Fankuchen (2), and others with the determination of the structures of substances which are gaseous or liquid at room temperatures from single crystal x-ray diffraction studies of these materials at low temperatures.

Summaries of advances in the determination of molecular structures by crystallographic, microwave absorption, and other spectroscopic procedures appear in other chapters of this volume. The bulk of this chapter is devoted to a review of structure determination by electron diffraction on vapors, and x-ray diffraction by liquids. The results obtained from other data have been compared with those based on electron diffraction measurements, where such comparisons proved illuminating. A few relatively new procedures are mentioned, even though these did not originate during the past year, because they have been omitted from previous reviews.

We have attempted to summarize the literature which appeared during the past year, starting at about the place where the previous reviewer (Brockway) terminated his report.

## PROGRESS IN THE TECHNIC OF ELECTRON DIFFRACTION OF GASES


During the past few years the use of rotating sectors has been widely accepted for reducing the range of electron intensity which has to be recorded in photographing diffraction patterns. Since the introduction of such sectors was first proposed in 1933 (3) and its practicability demonstrated in 1939 (4), one wonders why there has been so much inertia in going from the art of electron diffraction by "personal calibration" to the science of objective intensity measurements. The explanation, we believe, is that other developments were also necessary before the power of the sector technic could be fully exploited. Obviously, since in the equations used for the computation of theoretical intensity curves, it is postulated that single scattering occurs from a sample of infinitesimal extension, by a perfectly collimated beam, possession of precise intensity data for a scatterer, obtained under conditions which depart appreciably from the idealized ones listed is of relatively little help. Careful studies have now been reported (5 to 8) on nozzle design, vacuum, and beam focusing requirements. For any given set of conditions, the approximate magnitude of the disturbing effects due to multiple scattering and careless nozzle construction can now be estimated; optimum designs have been proposed.

Of equal importance is the need to follow a correct procedure for reducing the recorded intensity data to a form suitable for inversion, so that a quantitatively significant radial distribution curve results (9, 10, 11). It has long been appreciated that multiplication of the intensity pattern by one function of the angle, as the sector does, still leaves the intensity dependent in a somewhat involved fashion on the angular variations of the atom form factors. However, to obtain a radial distribution function which may be quantitatively interpreted in terms of interatomic distances and their vibrational displacements requires the inversion of data which would have been obtained were each atom to scatter in proportion to its atomic number, as a point of potential (atom form factor independent of angle). Recognition of the sensitivity of the final curve to the angular function which the sector leaves in the data has been a relatively recent development. A careful analysis of the various procedures which have been used to correct the data was made by Coffin, Bauer & Bregman (9); reliable methods for introducing these corrections are available. Extension of the scattering curve to zero angle, use of IBM computing machines, and recognition that termination of the integration at a finite angle (the maximum angle of the observed pattern) led to a "folded" rather than to the desired R.D. curve, are accomplishments of the group at the California Institute of Technology (12). Practical methods for deducing the "natural" from the "folded" peak shapes have been described by Karle (10) and by Coffin (9, 11). Finally, Coffin investigated the effects which various types of errors in the data have on the resulting R.D. curves. Hence, at present it is possible to record electron diffraction data accurately under conditions which approach those assumed in the theoretical equations,

reduce these data to absolute units for nuclear charge scattering, invert and obtain a radial distribution curve which is essentially positive everywhere and has no spurious peaks. The peaks which correspond to distances between pairs of bonded atoms have widths at half maximum of the order of 0.18 Å; well resolved peak positions are accurate to about 0.005 Å. Since for directly bonded pairs and for pairs one atom removed, the peaks are Gaussian in shape, it is possible to resolve superposed peaks, and to obtain moderately good estimates of the mean amplitude of vibrational motion. Typical results of several recent studies are cited below.

Keidel investigated the structures of toluene, phenylsilane, and diphenyl-dichlorosilane. A summary of the distances and mean vibrational amplitudes which he reported, and a comparison with those observed in related compounds are given in Table I. Attention is called to the precision which may now be claimed for structure determinations which are based on well resolved R.D. peaks. That these quoted limits of error are realistic is proved by the check obtained for the dimensions of the benzene ring between independent determinations (7, 13). Now it appears that whereas substitution of methyl, silyl, or phenyldichlorosilyl onto a benzene ring does not alter appreciably the  $(C-C)_{arom}$  distance, the ring angles probably do get distorted. Further, the  $C_r-CH_3$  and  $C_r-SiH_3$  distances are definitely less than in their alkyl analogues. These differences are somewhat larger than could be ascribed to hyperconjugation only. Results obtained by Karle & Karle on halogen substituted ethylenes are presented in Table II. Of particular interest is the comparison of the mean vibrational amplitudes observed with those computed by Morino *et al.* (19). For one molecule (marked with +), the discrepancy is much larger than the stated experimental error. Since the

TABLE I  
INTERATOMIC DISTANCES DETERMINED BY ELECTRON DIFFRACTION

Compound	$(C-C)_{ar}$	Si-C	Si-Cl		$\begin{cases} C-C \\ C-H \end{cases}$	Reference
$(C_6H_5)-CH_3$	1.39 <sub>2</sub> (.005)*	—sym. ring; assumed planar—			1.52 (.01) 1.11 (.02)	(7)
$C_6H_6$	1.39 <sub>2</sub> (.005)†	—sym. ring; $D_{6h}$ —			1.08 (.02)	(13)
$(C_6H_5)-SiH_3$	1.39 <sub>2</sub> (.005)‡	1.843 (.01)‡	—distorted ring; assumed planar—		1.10 (.02)	(7)
$SiMe_4$		1.89 (.02)‡			1.10 (.05)	(14)
$(Me_3SiO)_2$		1.88 (.04)				(15)
$(C_6H_5)-SiCl_3$	1.38 <sub>2</sub> (.01)	1.84 (.015)	2.05 <sub>2</sub> (.015)	3.19 (.03)		(7)
$Me_3SiCl_2$		1.83 (.06)‡	1.99 (.03)	3.12 (.06)		(16)
$Me_3SiCl$		1.89 (.03)‡	2.09 (.03)	3.17 (.03)		(17)

$(h_i^2)^{1/2}$  values (mean square variation in distance along line of centers) are reported as follows:

\* .049 ‡ .049




† .055 ‡ .040

‡ visual data. In case of  $SiMe_4$ , authors claim that their over-all temperature factor is consistent with assumed independent barrier of 1.3 kcal./mole height, for hindered rotation of methyl groups around Si-C bonds.

cumulative effects of errors in the data (multiple scattering, improper background corrections, etc.) tend to broaden the R.D. peaks, one may readily overestimate the precision of these determinations, and as easily explain why the observed values are always larger than the computed ones where a major discrepancy appears.

With the growth of confidence in the quantitative interpretation of the detailed features of the radial distribution curves, several electron diffraction analyses were made of compounds in which there is restricted rotation about a single bond. An early study was that reported by Hastings & Bauer (21) on the structures of neopentylchloride and silico-neopentylchloride. Although there was clear qualitative evidence that the barrier hindering rotation about the  $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{Cl}$  bond was considerably higher than that about the  $(\text{CH}_3)_3\text{Si}-\text{CH}_2\text{Cl}$ , no quantitative estimations were possible. In a recent study of 1,2-dichloroethane, Karle & Ainsworth (22) also did not attempt to deduce a value for the barrier height from the shape of the R.D. peaks ascribed to the  $\text{Cl}\cdots\text{Cl}$  interaction; rather they interpreted their data in terms of a mixture consisting of  $27 \pm 5$  per cent *gauche* form, the rest being *trans*. Incidentally, the value they report for the C—C distance ( $1.49 \pm .03$  Å) is surprising, in view of the almost complete masking of this small peak by the large C—Cl peak. At the present we see no simple procedure for estimating barrier heights directly from radial distribution curves, since a contribution of an unknown shape must be unscrambled from a region of the curve where there generally are many superposed peaks. This situation arose again in the case of  $\text{S}_2\text{F}_{10}$ , disulfurdecafluoride. As yet unpublished data on this compound (23) lead to a structure in which two octahedral ( $\text{SF}_6$ ) groups are joined by a S—S bond of length  $2.21 \pm 0.03$  Å. The average S—F distance is  $1.56 \pm .02$  Å, while the valence angles of the sulfur atoms are very

TABLE II  
INTERATOMIC DISTANCES AND AMPLITUDES OF VIBRATION FOR HALOETHYLENES

	C=C	C—X				C=C	Reference
$\text{C}_2\text{Cl}_4$	1.30 (.03)	1.72 (.01)	2.88 (.01)	3.18 (.02)			
$(l_{ij}^2)^{1/2}_{\text{obs.}}$		.048 (.005)	.070 (.01)	.125 (.01)			(18)
$\text{C}_2\text{F}_4$	1.31 (.03)	1.31 (.01)	2.20 (.02)	2.74 (.03)	3.51	2.31	(8)
$(l_{ij}^2)^{1/2}_{\text{obs.}}$		.056 (.005)	.087 (.01)	.090 (.01)	.114	.095	(8)
$(l_{ij}^2)^{1/2}_{\text{calc.}}$		.043 +	.055 +	.094	.057 +	.055 +	(19)
$\text{H}_3\text{C}=\text{CF}_3$	1.31 (.03)	1.32	2.16			2.33	(8)
$(l_{ij}^2)^{1/2}_{\text{obs.}}$		.042	.060			.060	(8)
$(l_{ij}^2)^{1/2}_{\text{calc.}}$		.044	.054			.057	(19)
$\text{C}_3\text{H}_4$	1.353						(20)



close to  $\pi/2$ . In spite of the unexpectedly long S—S distance, rotation of the  $\text{SF}_6$  groups about this bond is definitely hindered. An interesting comparison was made by Kisliuk & Silvey (24) of hindering potentials for three molecules, as determined from microwave absorption data (Table III). Their observations on  $\text{CF}_3\text{SF}_5$  are consistent with an octahedral configuration about the S atom, and a radius of 1.10 Å for sulfur (C—S 1.86 Å).

That barriers do hinder rotation about single bonds was suggested on the basis of visual electron diffraction data by Weir in 1932 (25). Since then various investigators observed that in order to obtain a good fit between their visual and computed intensity curves, several configurations must be mixed in reasonable proportions. In the case of 1,2-dichloropropane (26) the diffraction data alone proved insufficient to permit a complete description of the configurational arrangement; however, when these were combined with dipole moment data, a complete structure determination was possible.

TABLE III  
TORSIONAL POTENTIALS CALCULATED FROM MICROWAVE DATA

	Torsional Frequency ( $\text{cm}^{-1}$ )	Barrier Height ( $\text{cm}^{-1}$ )	Barrier Height (cal./mole)
$\text{CH}_3\text{CF}_3$	$230 \pm 10$	1200	3430
$\text{CH}_3\text{SiF}_3$	$140 \pm 30$	419	1200
$\text{CF}_3\text{SF}_5$	$93 \pm 25$	219	626

Concurrently, absolute configurations were assigned to the enantiomorphs of this compound on the basis of Kirkwood's theory of optical activity (27), which checked with the experimental conclusions. Thus, the Fischer convention was again confirmed as the correct representation of absolute configuration. The earlier confirmation by Bijvoet *et al.* (28) was based on an x-ray diffraction study of sodium rubidium *d*-tartrate.

*Remarks on rotational isomers (spectroscopic data).*—Early attempts to determine the structures of rotational isomers from infrared and Raman data were based on the application of selection rules to the symmetry requirements of the models, and on deductions of torsional frequencies from combination bands. These were not particularly successful. In recent studies, such data have been used primarily as a method of analysis for the isomers. By measuring the effect of temperature on the relative intensities of the spectra assigned to each isomer, the energy differences between their ground states (also their entropy differences) have been deduced in cases where one form is more stable than another. During the past year a number of papers appeared following this method of attack. Extensive references to previous work will be found therein. Typical data are listed in Table IV. Some indications of barrier heights are also obtained in this way.

It is conceivable that by combining these spectroscopic conclusions,

which give the necessary Boltzman terms for the computation of the composition of the vapors, with precise radial distribution curves, one may be able to arrive at a more detailed analysis of the shape of potential barriers hindering free rotation about single bonds.

TABLE IV  
ENERGY DIFFERENCES BETWEEN ISOMERIC FORMS

	More Stable Form	$\Delta E$	Reference
CH <sub>2</sub> OH—CH <sub>2</sub> Cl	<i>gauche</i> (OH—Cl)	0.95 $\pm$ .02 kcal./mole	(29), (30)
CH <sub>2</sub> Cl—COCl	<i>trans</i> (Cl—Cl)		(31)
CH <sub>2</sub> Br—COCl	<i>trans</i> (Br—Cl)	1.0 $\pm$ 0.1	(31)
CH <sub>2</sub> Br—COBr	<i>trans</i> (Br—Br)	1.9 $\pm$ 0.3	(31)
CHCl <sub>2</sub> —CH <sub>2</sub> Cl		$\cong$ 0.1	(32)
CHBr <sub>2</sub> —CH <sub>2</sub> Br		$\cong$ 0.5	(32)
CHCl <sub>2</sub> —CHCl <sub>2</sub>		not determinable	(32)
CHBr <sub>2</sub> —CHBr <sub>2</sub>			
ON—OH	<i>trans</i> (O—H)	0.506	(91)

#### PROGRESS IN THE THEORY OF ELECTRON DIFFRACTION

Perhaps the most significant development in this field in 1952 was the extension of the theoretical scattering formula beyond the first order Born approximation. The need for examining carefully the usually accepted equation when applied to very heavy atoms was suggested by Libby in 1944, in view of the contradictions regarding the structure of uranium hexafluoride, which appeared at that time. The data available in the literature which led to the apparently contradictory conclusions for the structures of the hexafluorides of molybdenum, tungsten, and uranium were summarized in 1951 (33). Whereas for these three molecules the diffraction experiments required two distinct distances, the spectroscopic, dielectric constant, and thermodynamic data unambiguously led to regular octahedral configurations. The impasse was resolved by Schomaker & Glauber (34). In the derivation of the expression for the scattered intensity one must sum over the scattered waves originating at the various atomic centers, each with its appropriate phase. In the first Born approximation, the wave function of the electron in the molecular system is assumed to be the undistorted (free electron) wave; this has been demonstrated (35) to be equivalent to the assumption that the scattering process at each center introduces only a very small phase change. However, if the phase changes are appreciable, then scattered intensity (to the second approximation) as a result of an atom pair includes a factor which is the cosine of the magnitude of the difference between the two phase changes. The above investigators used exponentially screened nuclei as atomic scatterers, and found that to the second approximation, the intensity of scattering by a pair is

$$2 |f_i(s)| |f_j(s)| \cos(s\delta) \frac{\sin sr_0}{sr_0}$$


where  $s$  is defined previously;  $r_0$  distance between atoms  $i$  and  $j$ ;  $|f_i(s)|$  is the absolute value for the scattered amplitude, and is assumed to be equal to the usual form;  $s\delta = |\eta_i(\theta) - \eta_j(\theta)|$  is the difference in phase changes due to scattering at  $i$  and  $j$ . At large angles,  $\delta$  depends on the difference in the logs of the screening parameters, and hence on the difference in atomic numbers. Thus the cosine factor introduces an apparent split in the distance of  $i$  from  $j$  of a magnitude which depends on the difference in their atomic numbers; for, on the basis of the first Born approximation, the intensity as a result of two pairs of atoms with separations  $(r_0 - \delta)$  and  $(r_0 + \delta)$  would reduce to just the expression given above. In a table given by Schomaker & Glauber, the apparent splits so computed agree very well with those reported for the three hexafluorides, and for a number of other molecules, for which they quote unpublished data. It appears, however, that a considerable amount of careful reinvestigation will have to be undertaken. Two examples may be cited. Tellurium hexafluoride, according to accepted electron diffraction results, has a regular octahedral configuration, whereas an apparent split of about 0.14 Å should have appeared; in iodine heptafluoride, an unsymmetrical split is observed of about 0.09 Å whereas this theory predicts a value of 0.15 Å.

A parallel theoretical analysis of this problem has been reported by Greenberg & Montroll (36, 37). Their treatment also leads to a cosine term in the expression for the intensity, but its argument is independent of  $s$ , which does not check with the observed intensity data for  $\text{UF}_6$  at small and intermediate angles.

#### RESULTS OF STRUCTURE DETERMINATIONS

*Compounds containing boron.*—In the current review of experimental crystallography, Lipscomb discussed most of the structural data which have been recently reported on compounds containing boron. Here we have quoted some unpublished electron diffraction data and a comment regarding these structures. The former are assembled in Table V, along with data on related compounds. The strictness of the analogy between the boron-nitrogen and aromatic systems with regard to the importance of Kekulé type resonance, which has generally been postulated, has been questioned by Pease (43). If one accepts the numbers in the table at face value, it follows that the ratios of the ring distances to the "single bond" distances are comparable for benzene, phenyl-boron dichloride, and the substituted borazoles, constituting one group; in another, one finds graphite, boron nitrite, and borazole. Further, the B—Cl distance in the B-trichlor substituted borazole definitely appears to be longer than that in boron trichloride. Hence, to account for all the data, one must take a judicious combination of all three electronic structures which Pease presented (43). It is of interest to mention

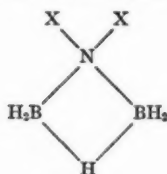
TABLE V  
INTERATOMIC DISTANCES IN SOME BORON COMPOUNDS

Compound	C—C B—N	B—Cl	B—C		$\left( \begin{array}{c} \text{C—C} \\ 1.545 \\ \text{B—N} \\ 1.554 \end{array} \right)$	Procedure	Reference
C <sub>6</sub> H <sub>6</sub>	1.393 (.01)				0.902	e.d. (sec.)	(13)
C <sub>6</sub> H <sub>5</sub> BCl <sub>2</sub>	1.38 (+.02) (−.01)	1.72 (.03)	1.52 (.07)	2.93 (.01) 118° (3)	0.895	e.d. (vis.)	(11)
H <sub>3</sub> B <sub>2</sub> N <sub>2</sub> H <sub>4</sub>	1.44 (.02)				0.927	e.d. (vis.)	(38)
Cl <sub>2</sub> B <sub>2</sub> N <sub>2</sub> H <sub>4</sub>	1.41 (.02) 1.413 (.01)	1.78 (.03) 1.760 (.015)			0.909	e.d. (vis.) x-r (cryst.)	(11) (39)
H <sub>3</sub> B <sub>2</sub> N <sub>2</sub> Me <sub>4</sub>	1.42 (.02)				0.908	e.d. (vis.)	(11)
BCl <sub>3</sub>		1.73 (.02)		3.00 (.02) 120°		e.d. (vis.)	(40)
BMe <sub>3</sub>			1.56 (.02)			e.d. (vis.)	(40)
H <sub>2</sub> BCO			1.540			μλ	(41)
BN	1.446				0.930	x-r (cryst.)	(42)

that the conjugation of the BCl<sub>2</sub> group with the ring is quite marked in phenyl borondichloride. This is suggested by the distances, which regretfully are not sufficiently precise. The strongest argument for this point is the large dipole moment observed (44),  $3.05 \pm .15$  D, which would follow from the polar structures introduced when the  $\pi$  electrons of the ring become donor electrons to the boron atom.

Part of the ambiguity in the formulation of resonance structures for these (B—N)<sub>2</sub> rings is due to the obvious difficulty of giving meaning to the term "normal single bond" between adjacent atoms, one of which is a good acceptor while the other is a good donor. This difficulty does not arise in the interpretation of the structure of the (B—N)<sub>2</sub> ring, present in the dimer of dimethyl aminoborane, (Me<sub>2</sub>N—BH<sub>2</sub>)<sub>2</sub>. This four membered ring is essentially planar (45), with the B—N distance comparable to that found in other such donor-acceptor compounds (46). Since the heat of dimerization of Me<sub>2</sub>N—BH<sub>2</sub> is only 20.6 kcal. (47) while the heat of complexing trimethylamine with borane is of the order 33 kcal. per B—N bond (48), it is obvious that the monomer unit is destabilized in the process, and this may be formulated in terms of loss of resonance with the ionic structure Me<sub>2</sub>N<sup>+</sup>=<sup>−</sup>BH<sub>2</sub>.

Another pair of compounds in which there appears to be a four membered ring is N-dimethylaminodiborane and aminodiborane, the structures of which have been investigated by Hedberg & Stosick (49). The configuration of the heavy atoms has been determined:



B—N	$1.55 \pm .026 \text{ \AA}$	$\angle \text{BNB}$	$76.4 \pm 5.5^\circ$	C—N	$1.48 \pm .03 \text{ \AA}$	(X=Me)
B—N	$1.56 \pm .026 \text{ \AA}$	$\angle \text{BNB}$	$76.2 \pm 2.8^\circ$			(X=H)

The position of the bridging hydrogen is surmised, from the unexpectedly small  $\angle \text{BNB}$ .

Much of the available data on the structures of these interesting compounds of boron have been assembled by Hedberg (50). He was able to correlate most of the observed interatomic distances with reasonable bond orders, using Pauling's relation  $D(I) - D(n) = 0.6 \log n$ , and assuming a boron bond radius of 0.80 for  $n$  unity. He also computed rough values for dipole moments of some of the boranes. A comparison of the values calculated by Hedberg with the ones observed experimentally show for  $\text{B}_5\text{H}_9$   $\mu_{\text{Hed}} = 1.1 D$ ,  $\mu_{\text{obs}} = 2.13 \pm 0.04 D$  (51), and for  $\text{B}_4\text{H}_{10}$ , 1.4 and  $3.52 \pm 0.02 D$  (52) respectively. The fact that these large values appear surprising to most investigators indicates how far we are from a satisfactory understanding of electron deficient compounds. We suggest that a partial explanation is that hydrogen has a much greater electronegativity than does boron, as proposed by Walsh (53).

*The halocarbons.*—During the past year precise data have been presented which prove that in the series mono- to tri-halogen substituted methanes, the carbon-halogen bond length is sequentially less, the effect being much more marked for fluorine than for chlorine. Electron diffraction (54) and microwave (55) data on difluoromethane gave for the C—F distance  $1.357 \pm 0.017 \text{ \AA}$  and  $1.358 \pm 0.001 \text{ \AA}$ , respectively, while for the  $\angle \text{FCF}$  the two methods gave  $107.5 \pm 1.5^\circ$  and  $108^\circ 17'$ . In the latter paper the available structural data on these substituted methanes were summarized; values for their dipole moments were included. Parallel with this work, Sheridan & Gordy (56) reported on the structures of various trifluoromethyl halides and cyanide. Whereas the C—F separations and the  $\angle \text{FCF}$  angles appear to be the same for all these compounds, the C—X distances are definitely less than in the corresponding methyl analogues, by an amount which gets progressively less in going from fluorine to iodine. Thus, in  $\text{F}_3\text{CX}$ , C—F =  $1.300 \pm .008 \text{ \AA}$  and the bond angle is  $108^\circ$ ; the C—X distances are 1.740, 1.908, 2.134, and  $1.464 \text{ \AA}$  (all  $\pm .02 \text{ \AA}$ ) for the sequence, C—Cl, C—Br, C—I, and C—CN. An electron diffraction investigation of ketene, carbonyl-fluoride, and tetrafluorethylene was undertaken by Broun & Livingston (57) to permit a comparison of their C—F separations, and to determine the effect of the substitution of fluorine on the other interatomic distances in these molecules. Their results are summarized in Table VI (also, cf. Table II). As mentioned in the introduction, Sheehan & Schomaker (59) found the

distances and bond angles in perfluorobutyne-2 to equal the corresponding ones in trifluoromethyl acetylene. For C—F they gave  $1.34 \pm 0.02$  Å and  $\angle \text{FCF } 107\frac{1}{2} \pm 1^\circ$ . That the successive replacement of hydrogen by fluorine has a profound influence on the electron distribution in the molecule as a whole can no longer be doubted. The effect shows up in the observed bond energies and in the appearance potentials of ions in mass spectra (60). In our opinion, no simple satisfactory explanation has yet been given (33); it is evident, however, that changes in bond hybridization must be considered (61).

TABLE VI  
INTERATOMIC DISTANCES IN KETENE AND RELATED COMPOUNDS

	C=C	C=O	C—F	$\angle \text{HCH}$ $\angle \text{FCF}$
H <sub>2</sub> C=CO (e.d.)	1.30 (.02) Å	1.16 (.02) Å		
H <sub>2</sub> C=CO ( $\mu\lambda$ , 58)	1.31 <sub>6</sub> (.01)	1.16 (.01)		122 (2.5) <sup>o</sup>
F <sub>2</sub> C=O		1.17 (.02)	1.32 (.02) Å	112 $\frac{1}{2}$ (6) <sup>o</sup>
F <sub>2</sub> C=CF <sub>2</sub>	1.33 (.06)		1.30 (.02)	114 (3) <sup>o</sup>

Reinvestigation of some of the saturated perfluorocarbons has shown that the effects of fluorine substitution on the adjacent C—C distances are of much smaller magnitude than was initially suggested by Brockway & Livingston (62). Livingston & Brandt (63) reported that the C—C separation in perfluoroethane is  $1.52 \pm .05$  Å, in agreement with the lower limit for this distance given by Bauer & Beach (64). In both analyses, the torsional motion of the CF<sub>3</sub> groups was taken into consideration in computing the theoretical intensity curves. For C—F, they gave  $1.33 \pm 0.01_5$  Å. The structures of dodecafluoro-*n*-pentane, hexadecafluoro-*n*-heptane and dodecafluoroisopentane have been determined by Bastiansen & Hadler (65) who used a sector in their electron diffraction study. In all three cases they observed C—F = 1.38 Å, restricted rotation about the C—C bonds, with the most stable configuration being a zigzag chain.

*Structures of other organic molecules.*—Dunitz *et al.* (66) investigated the structure of the very interesting substance, cyclopropene. They found: C—C  $1.52_5 \pm 0.02$  Å; C=C  $1.29 \pm 0.04$  Å; an average value for C—H  $1.09 \pm 0.04$  Å; of course, confirming the cyclic structure for the compound. The shorter than "normal" interatomic distances are in agreement with this previously reported observation for the three-membered ring systems: spiropentane, cyclopropane, ethylene oxide, and ethylene sulfide (67). Further support was afforded by the electron diffraction study of 1,1,2,2-tetramethylcyclopropane (68), for which an average C—C distance of  $1.52 \pm 0.03$  Å was reported, with  $114 \pm 6^\circ$  for the external angle, Me—C—Me. The molar diamagnetic susceptibilities of cyclopropane, ethylene, and propylene oxides are unusually large, being 8.6 units greater than the corresponding straight chain isomer (69). One may argue that this lends some

support to the explanation offered by Walsh (70) for the electronic structures of the three membered ring compounds. The trigonal wave functions at each carbon atom are extended in the plane of the ring, thus giving a large  $\langle r^2 \rangle_{av}$  even though overlap requirements bring the atomic centers close together.

In contrast, the C—C distances in the four membered rings appear to be larger than in the chain hydrocarbons. An electron diffraction study of cyclobutane by Dunitz and Schomaker (71) gave the following bond distances and angles: C—C  $1.56 \pm 0.02$  Å; C—H  $1.10 \pm 0.04$  Å and  $\angle \text{HCH}$   $114 \pm 8^\circ$ . Further, on the average the carbon atoms are not coplanar. They suggest that the potential energy arising from repulsion of nonbonded carbon atoms may contribute significantly to the apparent high strain energy of cyclobutane, whereas no such repulsion is present in cyclopropane. Previously, in methylenecyclobutane [Bauer & Beach (72); Shand *et al.* (73)] reported that  $(\text{C—C})_{\text{ring}} = 1.56 \pm 0.03$  Å, and recently Lemaire & Livingston (74) found in methylcyclobutane  $(\text{C—C})_{\text{ring}} = 1.56 \pm 0.03$  Å; also, the angle between the side chain bond direction and the bisector of the adjoining C—C—C angle in the ring was assigned the value  $130 \pm 8^\circ$ . Lemaire & Livingston also reinvestigated octafluorocyclobutane. The ring is not planar, probably because of the repulsion between fluorine atoms attached to different carbons, with C—F  $1.33 \pm 0.02$  Å; C—C  $1.60 \pm .04$  Å and  $\angle \text{FCF}$   $109 \frac{1}{2} \pm 3^\circ$ . The C—C—C angles in the ring are about  $89^\circ$ .

Since diketene was prepared for the first time, nearly half a century ago, its molecular struture has been under dispute. During the past five years a large variety of technics have been brought to bear on this problem. Although chemical, spectroscopic, and electron diffraction (75) studies individually could give no unequivocal answer, collectively they strongly argued for the vinylaceto- $\beta$ -lactone structure. This has now been definitely established by an x-ray diffraction analysis of single crystals at low temperatures [Katz & Lipscomb (76)]. The ring was found to be planar, with C—O  $1.39$ – $1.40$  Å; C—C  $1.46$ – $1.48$  Å; and C=C, C=O  $1.35$ ,  $1.24$  Å, respectively (distances determined to  $\pm 0.06$  Å). Besides investigating the structure of ketene dimer, via the sector technic, Bregman (75) also studied  $\beta$ -propiolactone, methylketene dimer, and dimethylketene dimer. With regard to the latter, she confirmed the conclusions of Lipscomb & Schomaker (77). In the simple lactone the ring is planar with C—C  $1.54$  Å; C—O  $1.46 \pm .02$  Å; C=O  $1.21 \pm .02$  Å;  $(\angle \text{COC})_{\text{ring}} = 89 \pm 2^\circ$ . As a result of the large number of parameters, the only conclusion which could be reached regarding methylketene dimer is that a structure of the vinylaceto- $\beta$ -lactone type, with ring dimensions as in diketene, are in agreement with the data.

Bastiansen carried out an electron diffraction study of 1,3,5-triphenylbenzene, to determine the deviation of the molecule from coplanarity (78). He found that the angle between adjacent ring planes is  $46 \pm 5^\circ$ . Dipole moment measurements by Bastiansen & Markali (79) and an electron diffraction investigation by Bastiansen (80) of the five isomers of benzene-1,2,3,4-tetrachloride show that they have the following molecular configurations:

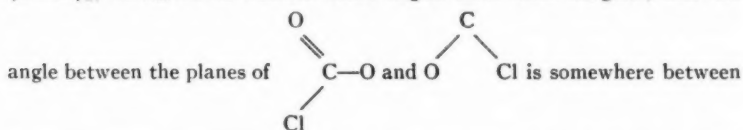


$\alpha(\epsilon\epsilon\kappa\kappa)$ ;  $\beta(\epsilon\kappa\kappa\epsilon \rightarrow \kappa\epsilon\epsilon\kappa)$ ;  $\gamma(\epsilon\kappa\kappa\kappa)$ ;  $\delta(\kappa\kappa\kappa\kappa)$ ;  $\epsilon(\kappa\epsilon\kappa\kappa)$ , where  $\epsilon$  stands for polar and  $\kappa$  for the equatorial locations. The infrared spectra of cyanuric acid and deuterocyanuric acid were published by Newman & Badger (81). The results indicate the equivalence of all the C=O bonds, in disagreement with an earlier x-ray structure determination. However, a reinvestigation by Wiebenga (82) of the crystal structure showed that the spectroscopic conclusions were correct. The C=O distance is 1.21 Å.

Extensive efforts have been made to determine the structure of cyclooctatetraene. Three atomic arrangements have been proposed with symmetries  $D_{2d}$ ,  $D_4$  and  $D_{4d}$ . Spectroscopic, electron, and x-ray diffraction techniques have been applied. A sector-electron diffraction study of the vapor by Karle (13) led to  $D_{2d}$  (tub) configuration; the horizontal C—C bond lengths are  $1.35 \pm 0.01$  Å, and the oblique C—C bonds are  $1.50 \pm 0.01$  Å. Person, *et al.* (83) believe that potential energy considerations based on data for related hydrocarbons confirm this symmetry.

The molecular structure of acetone finally has been removed from an area of disagreement. Independent studies in four laboratories using both the sector and visual technics (84, 85, 86) gave the following average values: C=O  $1.23 \pm .03$  Å; C—C  $1.55 \pm .02$  Å;  $\angle$ CCO  $121 \pm 3^\circ$ .

The structure of the carboxylic ester group has been further investigated in an electron diffraction analysis of gaseous monochloromethyl chlorformate (87). The reported distances are: C=O  $1.20 \pm .03$  Å; (C—O)<sub>av</sub>  $1.40 \pm .04$  Å; (C—Cl)<sub>av</sub>  $1.74 \pm .02$  Å. Various bond angles have been assigned, and the



$0^\circ$  to  $90^\circ$ , with the chlorine atoms in the  $\text{CH}_2\text{Cl}$  unit *trans* to the carboxyl carbon atom.

Previous work on various methyl derivatives of acetylene, for which both electron diffraction and spectroscopic methods have been used, showed the C—C bond distance to be considerably shorter than the expected 1.54 Å. Besides the effect arising from the use of *sp* hybridization, the shortening has been explained as resulting partly from hyperconjugation of the  $\text{X}_3\text{C}\equiv\text{C}$ — group with the triple bond. For comparison, the distances reported this year are listed in Table VII.

Interesting structural data in the infrared on several compounds containing nitrogen were obtained by Badger and co-workers. Gaseous nitrous acid (91) exists in two tautomeric forms, with the *trans* being more stable than the *cis* by 506 cal./mole. Reading the formula as HONO, probable values for the distances are: H—O 0.98 Å; O—N 1.46 Å; N—O 1.20 Å; with the bond angles,  $\angle$ HON  $103\text{--}105^\circ$ ;  $\angle$ NON  $114\text{--}118^\circ$ . A careful study was made of the chloramines and nitrogen trichloride (92). By combining the large moments of inertia which were evaluated in this work with previous structural data on closely related compounds, these authors concluded that in



$\text{NH}_2\text{Cl}$  the angle  $\angle\text{HNCI}$  is  $102^\circ$ ; in  $\text{NHCl}_2$  is  $106^\circ$ , while the  $\text{N}-\text{Cl}$  distance is  $1.76 \text{ \AA}$ . The latter has been measured in  $\text{Me}_2\text{NCl}$  to be  $1.77 \pm 0.02 \text{ \AA}$  by electron diffraction (93). Finally, the conclusion was reached that the normal valence bond angle for nitrogen is  $102^\circ$ , in agreement with the previous suggestion of Schomaker & Lu.

TABLE VII  
INTERATOMIC DISTANCES IN ACETYLENE DERIVATIVES

	C—C	C $\equiv$ C	C—H	C—X	Reference
$\text{HC}\equiv\text{CH}$		1,208 <sub>a</sub>	1,057 <sub>a</sub>		(88)
$\text{H}_3\text{C}-\text{C}\equiv\text{CH}$	$1,467 \pm 0,003$				(89)
$\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CH}_3$	1,37 <sub>a</sub>	1,207 (*)			(89)
$\text{H}_3\text{C}-\text{C}\equiv\text{CBr}$	$1,46 \pm 0,02$	1,207 (*)	1,092 (*)	$1,793 \pm 0,005$	(90)
$\text{H}_3\text{C}-\text{C}\equiv\text{CI}$	$1,46 \pm 0,02$ (*)	1,207 (*)	1,092 (*)	1,99	(90)
$\text{F}_3\text{C}-\text{C}\equiv\text{C}-\text{CF}_3$	$1,46 \pm 0,06$ (*)	$1,22 \pm 0,09$		$1,34 \pm 0,020$	(59)

(\*) Assumed.

#### X-RAY DIFFRACTION STUDIES OF LIQUIDS AND SOLUTIONS

Wood & Ritter (94, 95, 96) have embarked on a programmatic investigation of fused salt systems by x-ray diffraction. In their first paper they described their vacuum camera, crystal monochromator, and the adoption of the Warren-Krutter-Morningstar (97) method for deducing a radial distribution function for a heteroatomic liquid. For liquid aluminum chloride, in the region of short interatomic distances, their R.D. curve was compatible with a structure for the dimer which agreed well with that determined by Palmer & Elliott (98) from electron diffraction by the vapor. They next studied fused indium tri-iodide and concluded that there is tetrahedral coordination of iodine atoms around the indium atoms, with the  $\text{In}-\text{I}$  distance  $2.70 \text{ \AA}$ . They could not determine whether monomers or dimers predominate, although both are present; further, they proposed a structure for the dimer similar to that for aluminum chloride. In their latest paper, studies of molten tin tetraiodide are reported. They found evidence for independent tetrahedra, with the  $\text{Sn}-\text{I}$  bond distance  $2.66 \text{ \AA}$ . Since these investigators used diffraction data which could be extended to an  $s$  value of eight to nine only, there is a serious question whether an inversion which can be interpreted in detail can be derived from such limited data (11). It is worth emphasizing that one of the steps in the reduction of the data requires the dividing of the observed intensities at the large angles by the sum of the atom form factors, both numerator and denominator being small quantities and subject to a high relative error. Nevertheless, a number of interesting conclusions regarding the structures of fused salts will be derived from these studies.

Investigation of salt solutions by Vaughan *et al.* (99) were based on the postulate that the x-ray diffraction pattern produced by a solution of a strongly scattering solute in a weakly scattering solvent approximates closely the pattern from a gas of the solute molecules.<sup>2</sup> They used crystal monochro-

matized tungsten  $K\alpha$  radiation, and reported patterns which extended to  $s=14.5$ . The photographs were analyzed by a visual technic, similar to that used in electron diffraction procedures. Water solutions of complex halogen anions of platinum, niobium, and tantalum were thus studied. In chloroplatinic and bromoplatinic acids, the  $PtX_6$  group was found to be octahedral; the Pt—Br distance is 2.43 Å, in agreement with the sum of radii, while a rough value for the Pt—Cl distance is 2.39 Å. In the  $M_6X_{12}$  complexes of niobium and tantalum, the six metal atoms form a regular octahedron (Nb—Nb 2.9 Å) with the 12 halogen atoms placed at radial perpendicular bisectors of the octahedral edges (shortest Nb—Cl 2.4 Å). For the tantalum complexes, Ta—Ta = 2.9 Å, Ta—Br =  $2.62 \pm .07$  Å; Ta—Cl =  $2.44 \pm .10$  Å.

Finally we wish to mention the work of Michelsen on the diffraction of x-rays by aqueous solutions of ammonium nitrate (100) and perchloric acid (101). In the salt solution his radial distribution curves showed maxima at 1.33 and 2.1 Å which he attributed to N—O and O—O distances in the nitrate ion, respectively (they are 1.25 Å and 2.2 Å in the crystal). An interesting conclusion followed from the fact that the R.D. peaks of water were shifted as a consequence of the introduction of the salt. These displacements Michelsen interpreted in terms of hydrogen bond formation between an oxygen from  $NO_3^-$  and  $NH_4^+$  or water molecules. He confirmed the tetrahedral configuration for the perchlorate ion, and cites 1.49 Å as the distance for Cl—O. Here also hydrogen bonding between perchlorate ions and water, and between several ions by water bridges is supposed to occur.

#### SOMEWHAT NOVEL PROCEDURES FOR STRUCTURE DETERMINATION

As a result of painstaking developments of the electric resonance method of molecular beam spectroscopy, there became available another tool for measuring interatomic distances and dipole moments of some molecules in selected vibrational and rotational states, just as is the case for structural determinations from microwave absorption studies. Consideration of the variations in quantities which have been regarded as "molecular constants" with the degree of thermal excitation has already raised some interesting problems (102), and more will follow. The most recent molecular beam studies have been reported by Trischka (103) on cesium chloride. The available data on the structures of the alkali halides in the vapor state are summarized

<sup>2</sup> This assumption is hardly justified. Even if one were to neglect completely the diffraction by the solvent, he must not neglect the contribution arising from solute-solvent interaction. For example, consider the case of  $PtBr_6^{2-}$  in water. For purposes of estimation, assume that the atom form factors are proportional to the atomic numbers; then the contribution of an atom pair to the pattern at any value of  $s$  is  $Z_i Z_j / r_{ij}$ . Hence, each complex ion contributes 11,750 units. However, if one makes the reasonable postulate that there are 18 oxygen atoms in the first water coordination sphere around this large ion, three for each Br atom, and 18 for the Pt atom, the contribution arising from placing this single layer of water around the  $PtBr_6^{2-}$  ion is in excess of 5000 units.

in Table VIII. Theoretical calculations of the  $r_e$  values for these substances have been made by Rittner (107). In the case of thallous chloride, the microwave spectrum showed too many lines to be attributable to a diatomic molecule (108); hence complexes of this salt are suspected of being present in the vapor at 305°C.

The exploitation of the mass spectrometer as a tool for structure determination is just getting underway. As was the case in the early spectroscopic determinations, the current procedures are essentially empirical. Morrison & Nicholson (109) reported on the ionization potentials of 83 organic molecules. They observed trends in the data arising from the presence of characteristic structural units, and were able to arrive at some generalizations regarding the effect of the ionization potential of the presence of double and triple bonds, and of various functional groups.

TABLE VIII  
COMPARISON OF INTERATOMIC DISTANCES IN ALKALI HALIDES OBTAINED BY  
VARIOUS METHODS

	Vapor e.d. (104)	Crystal x-r (104)	Vapor mol. beam (105)	Elec. Mom. mol. beam	Vapor $\mu\lambda$ (106)
NaCl	$2.51 \pm .03 \text{ \AA}$	$2.814 \text{ \AA}$			$2.3606 \pm .0003 \text{ \AA}$ (j 1→2)
KCl	$2.79 \pm .02$	3.139	$2.67 \text{ \AA}$	10.6 D	checks mol. beam
RbCl	$2.89 \pm .01$	3.27			
CsCl	$3.06 \pm .03$	3.560	$2.88 (.03)$	10.46	$2.9041 \pm .0003$ (j 5→6)
KF		2.67	2.55	7.3	
CsF			2.35	7.9	

A careful study has been made of the dissociation of cyclopropane under electron impact (110) and a very interesting analysis of the mass spectra of six lactones has been reported by Freedman & Long (111). The fragmentation process for such ring compounds appears to follow a characteristic pattern; in particular, the probability is quite high for getting two fragments resulting from the breaking of alternate bonds in the lactone ring. This typical behavior was then used to ascertain that the structure of ketene dimer in the vapor phase is vinylaceto- $\beta$ -lactone, as indicated by electron diffraction studies (75), and demonstrated by x-ray diffraction analysis of the crystals at low temperatures (76). Additional information was gained from the mass spectra, to the effect that if another isomer were present in the vapor (as was suggested by the infrared data), the concentration of the latter must be quite small.

Another physical measurement has recently been added to the roster of quantities which may be correlated with molecular structure, the velocity of propagation of ultrasonic waves in liquids. Efforts to calculate empirically the velocity of sound by summing bond increments to deduce a "molar sound velocity" for molecules in the liquid phase have only been partly successful. The reader is referred to a recent book by Vigoureaux (112), and to a brief

paper by Lagemann, *et al.* (113) where references to previous compilations are given.

#### CONCLUDING REMARKS

Throughout the above review we have used the term molecular structure to refer to the geometrical configurations of atomic centers in molecular units. The divorcing of such data from what is often referred to as the electronic structure of molecules is not only arbitrary, but if consistently maintained, will leave the geometrical information with relatively little interpretative value to the chemist. However, it is worthwhile to point out that whereas the connexity between atoms in a molecule must be known to permit complete identification of that molecular species, and the interatomic distances are needed to the precision now generally attained in diffraction studies for the computation of thermodynamic functions, such data are relatively crude as indirect measures of bond type, in the valence theory sense. The precision of molecular geodetics has been greatly improved with the study of rotation spectra, but the indirect nature of the relation between interatomic distances and details of bonding are not readily circumvented. To deduce the more detailed distributions of charge, to obtain some rough notions of the shapes of molecular electron wave functions, angular momenta and energy levels, one must use a larger variety of probes than has been listed above. Such data are slowly being accumulated. The magnitudes of permanent dipole moments, magnetic susceptibilities, force constants, polarizability, quadrapole coupling constants, ultraviolet absorption spectra, etc. all present different aspects of the electronic structure. So far, only the electron density maps resulting from careful fourier analysis of single crystal data, give a direct though as yet not sufficiently precise measure of the distribution of charge in condensed molecules, when these are in their ground electronic states. Hence, in concluding this review of experimental molecular structure we shall call attention to two recent papers to serve as an example of the more diverse type of structural investigation which are of interest to chemists.

From the intensities of absorption in the infrared (or from dispersion in the infrared) one can deduce the magnitudes of dipole moments associated with characteristic molecular vibrations, which for sufficiently simple molecules may be expressed as dipole moments assigned to individual bonds. Such bond moments being direct measures of the asymmetry of charge distribution in a region involving pairs of atoms, are magnitudes which a satisfactory valence theory must properly interpret. The dispersion data obtained by Rollefson *et al.* (115) now permit a comparison of the C—H bond moments in methane, ethylene, and acetylene. These are: 0.307D, 0.629 D, and 1.05 D, respectively. These large variations must be a result of significant differences in the nature of the bonding wavefunctions of the tetra-, tri-, and bi-coordinated carbon atoms; the corresponding C—H bond distances differ only slightly (115).

The subject of bond moments is the basis of a general paper by Mecke (116), in which he discusses the usefulness of infrared intensity data in obtaining measures of character of chemical binding.

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## EXPERIMENTAL CRYSTALLOGRAPHY<sup>1</sup>

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The present selection of papers admittedly reflects the background and interests of the writer, even though some attempt towards a balanced discussion, partly related to recently published reviews, has been made. A review of one single year occasionally necessitates the omission of significant contributions to extended programs, in the expectation that a subsequent reviewer will pick up these threads and weave them into a pattern different from the present one. For those papers selected here an attempt has usually been made to provide continuity with related chemical or physical-chemical problems.

Although an extended discussion of methods is omitted here, the attention of the reader must be called to two articles of interest. The first is last year's review by Zachariasen, who discusses and applies (1) the statistical method of Sayre (2) and Cochrane (3) in a case where the interpretation of the three-dimensional Patterson function did not yield the structure. The second is the long-awaited report of the Conference held April 6 to 8, 1950 at Pennsylvania State College entitled "Computing Methods and the Phase Problem in X-Ray Crystal Analysis" (4); this report contains a thorough discussion of all parts of the phase problem. It is worthy of observation that the power of the three-dimensional Patterson function for the elucidation of trial structures of molecules and crystals is only now being fully realized [cf. Donohue & Trueblood, (5)], and still represents, perhaps, the most powerful tool of the practicing crystallographer.

### ORGANIC STRUCTURES

The elucidation of complete molecular structures of relatively complex organic compounds, often by methods which require a minimum of chemical information, by x-ray diffraction techniques has been one of the most significant advances in recent years. The total effort in man hours required for such a complete structure determination is sometimes less than that expended in the determination of the molecular structure by the more classical organic methods. Lack of realization of this fact by most organic chemists is matched only by the reluctance of most crystallographers to undertake such investigations. The most striking of the early successes of this method was the elucidation of the then unknown molecular structure of phthalocyanine [Robertson (6)] and some of its isomorphous heavy metal salts, a study which remained almost unique for some years.

The recent appearance of a refinement of the potassium benzyl penicillin structure by Pitt (7) reminds us of the remarkable earlier study, which it

<sup>1</sup> The survey of the literature pertaining to this review was concluded in December, 1952.



confirms, by Crowfoot *et al.* (8). It is sufficient to recall the importance of this earlier study in establishing the presence of the four-membered oxazalone ring in the structure.

The correctness of the Fischer convention for the absolute configuration of an optical isomer was unambiguously established by Bijvoet, Peerdemann & van Bommel (9), who employed the known phase shift near the rubidium  $K$  absorption edge to destroy the center of symmetry in reciprocal space. The interaction of this phase shift with the phases of the diffracted rays allowed a correlation of the noncentrosymmetric pattern with the absolute configuration of the tartrate ion in sodium rubidium D-tartrate. The correctness of the Fischer convention has now been established independently by a theory of optical rotatory power in an investigation by Wood, Fickett & Kirkwood (10).

Although the remarkably detailed electron density maps of naphthalene [Abrahams, Robertson & White (11)] and anthracene [Sinclair, Robertson & Mathieson (12)] appeared a few years ago, a discussion of the results continues. Corrections for termination of the finite series, not made by the original authors, have been evaluated by Ahmed & Cruickshank (13), and further comparison of the experimental results with the results of valence theories have been made by Coulson, Daudel & Robertson (14). The different C—C distances in various parts of these molecules can be said to be established experimentally and to be understood on a theoretical basis, within the present standard deviations of  $\pm 0.005$  to  $0.010\text{\AA}$ . The precision of such studies suggests that, with the use of more accurate intensities now obtainable by nonphotographic techniques, results may be obtainable in the near future showing details of electron densities sufficiently accurate to provide an experimental guide to modern valence theories [cf. March (15)].

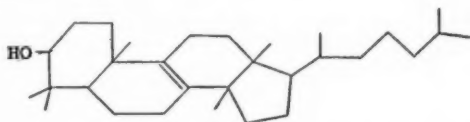
The two independent determinations of the molecular structure of the strychnine molecule appeared in 1951 [Robertson & Beevers (16); Bokhoven, Schoone & Bijvoet (17)]. These two investigations were begun before the structure was established by organic methods and were completed subsequently. It is important, however, and indicative of the present trend in the determination of molecular structures of such large molecules, that no chemical assumptions were made in these determinations; only the x-ray evidence was needed. Also interesting is the fact that these two studies were made on different salts and by entirely different treatments of the x-ray data.

The complex between urea and the normal hydrocarbons is the subject of a complete structure determination by Smith (18), who made a different type of direct analysis with no chemical assumptions in the initial stages.<sup>2</sup>

<sup>2</sup> This method, applicable to projections along certain axes of symmetry, is that described by Buerger (19, 20) as the implication diagram. In this application the Patterson-Harker section  $P(x\ y\ \frac{1}{2})$  is the projection of the electron density along the  $6_1$  axis, and the Fourier map is thus obtained directly from the observed data without the usual intermediate step of determination of a trial structure of the relative phases of the Fourier coefficients.

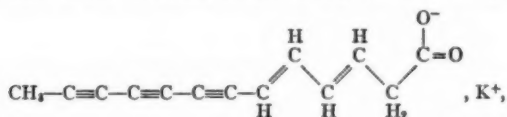
The crystal structure provides a sound structural understanding of the mechanism by which the formation of this complex separates the normal hydrocarbons, which fit into the structure, from the branched hydrocarbons, which do not. These molecular complexes resemble the clathrate compounds, structures of which have recently been elucidated by Powell and co-workers (21). A remarkable newly studied stable complex of this type is  $\text{Ni}(\text{CN})_2\text{NH}_3 \cdot \text{C}_6\text{H}_6$ , in which the benzene molecules are physically trapped; this complex has Ni in both the octahedral and the square coplanar configuration [Rayner & Powell (22)]. The hydrates of the rare gases, halogens, and other small molecules, referred to below, have molecular interactions which are very similar to the interactions in these organic complexes.

Some of the major problems presented by the unknown ring structures of the triterpenes have been solved by a determination of the crystal structure of lanostenol iodoacetate [Curtis, Fridrickson & Mathieson (23)]. The molecular structure



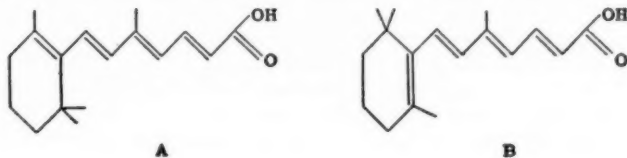
has also been arrived at independently by relatively straightforward organic methods very recently [Jager (24)]. The remaining problems of the triterpenes would be considerably advanced by a similar attack on the elemi acids, which have closely related molecular and crystallographic structures.

The problem of the molecular structure of potassium isomycomycin,



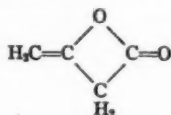
was also solved simultaneously and independently by x-ray diffraction analysis [Whitehouse, Eiland & Pepinsky (25)] and by organic techniques [Colmer & Solomons (26)]. Similar studies have been published showing complete molecular structure determinations of ergine [deVries & Pepinsky (27)] and colchicine [King, deVries & Pepinsky (28)] both of which confirm the structures derived by organic methods.

As a crystallographic contribution to the stereochemistry of the isomerism of the carotenoids, the molecular structure of *trans*- $\beta$ -ionylidene crotonic



acid has been shown to have the configuration (A) instead of the "conventional" formula (B) which has the type of steric difficulties discussed for the carotenoids by Pauling (30). This study was carried out by MacGillavry, Kreuger & Eichhorn (29) and establishes a configuration advocated previously only on not too convincing spectroscopic and steric evidence by Braude *et al.* (31).

The structure of diketene has been shown to be



from an x-ray diffraction study of a single crystal [Katz & Lipscomb (32)], thus establishing uniquely a molecular structure which was chiefly in doubt as a result of the failure of other physical methods and because of an incorrect earlier identification of the products of the ozonolysis reaction. The present structure is in agreement with all of the later-published evidence, but an equilibrium may be present at higher temperatures [Miller & Koch (33)].

The discovery of bis-cyclopentadienyl iron,  $(C_5H_5)_2Fe$ , a molecular compound of unusual structural interest, was reported during 1951 [Kealy & Paulson (34); Miller, Tebbboth & Tremaine (35)]. Unusual sandwich-type of structures having symmetry  $D_{5d}$  or  $D_{5h}$  (Fig. 1) were proposed by Wilkinson *et al.* (36), on the basis of the zero dipole moment,

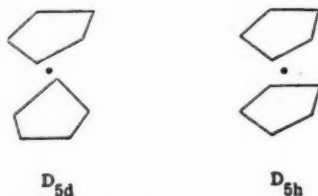


FIG. 1. Proposed structures for  $(C_5H_5)_2Fe$ .

diamagnetism and the single C—H stretching frequency at  $3.25\mu$ . Two independent crystallographic investigations have established that the  $D_{5d}$  model is correct [Dunitz & Orgel (37); Eiland & Pepinsky (38)]. The presence of only two molecules in the ubiquitous space group  $P2_1/a$  allowed unique establishment of the structure without any chemical assumptions and required the molecule to have a center of symmetry. The nature of the bonding between Fe and C ( $2.0\text{\AA}$ ) is described from a qualitative molecular orbital point of view by Dunitz & Orgel and leads naturally to an interpretation of the observed diamagnetism. The bonding is distributed among a larger number of nearest neighbors than that observed in the silver ion-benzene complex ( $Ag-C = 2.6\text{\AA}$ ) in silver perchlorate-benzene crystals [Rundle &

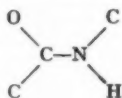
Goring (39)]. It may be hoped that the elucidation of these and related complexes will contribute to the general theory of molecular complexes [Mulliken (40)].

#### AMINO ACIDS, RELATED COMPOUNDS, AND PROTEINS

In a very detailed study of the structure of hydroxyl-L-proline by Donohue & Trueblood (41), the zwitterion type of molecular structure was established in disagreement with Zussman's (42) less accurate but otherwise qualitatively similar results, and the relative configuration of the  $\alpha$ -carbon and the carbon which carries the hydroxyl group have been established unambiguously to be the same as that proposed by chemical methods [Neuberger (43)]. This work is a continuation of the program at the California Institute of Technology on the structures of amino acids and related compounds and refers to the earlier detailed studies of diketopiperazine,  $\alpha$ -glycine, DL-alanine,  $\beta$ -glycylglycine, N-acetylglycine, and L-threonine. Work is now completed or in press from this group on serine,  $\alpha$ -glycylglycine, N,N'-diglycylcystine, glycylglycylglycine, and glycylasparagine. Less accurate interatomic distances are available from studies made in the presence of heavy atoms, but molecular configurations have been established for cysteyleglycine from a study of its sodium iodide complex by Dyer (44) and for proline from a study of copper DL-proline dihydrate by Mathieson & Welsh (45); the proline configuration is the same as that found by Donohue & Trueblood.

The precision of these studies has allowed the formulation of principles for the configurations of proteins and related large molecular weight compounds [Pauling & Corey (46, 47); Pauling, Corey & Branson (48)], of which an excellent review by Perutz (49) has been published. Additional, but much shorter, descriptions of the present situation have been published by Edsall (50) and by Bragg (51). Related developments which appeared during 1952 are briefly discussed here.

The question of the planarity of the amide group



has received considerable discussion. In addition to the structures of the similar molecules discussed above, there is additional evidence of the planarity in other structures. The structure of N-methyl acetamide shows the planar amide group [Post, Holtzberg & Fankuchen (52)], a conclusion which is also indicated by the infrared spectra of some amino acid substituted N-methyl acetamides [Mizushima *et al.* (53)]. Mizushima & Shimanouchi (54) have also discussed the relation of configuration to the potential barriers to internal rotation in polypeptide chains.

The question of the amount of energy required to strain the amide group into a slightly nonplanar configuration, discussed by Pauling & Corey

(55), is of importance because of the description of two new spiral models for polypeptides. The more promising is the  $\pi$ -helix discovered by Low & Baybutt (56); this helix is intermediate between the  $\alpha$  and  $\gamma$  helices [Pauling, Corey & Branson (48)] in that it has 4.4 amino acid residues per turn. The distortion of the intrachain  $\alpha$ -carbon bond angle is slightly less than  $5^\circ$ , and the corresponding strain energy may easily be overcome by other factors. The second new helix is the 11-atom helix, described by Huggins (57). The significant strain energy in this helix, estimated to be 6 kcal./mole (55), is associated with the nonplanarity of the amide group.

The evidence for the validity of the  $\alpha$ -helix (48) in the synthetic polypeptide, poly- $\gamma$ -methyl-L-glutamate, continues to be very favorable indeed. A hexagonal unit with  $a = 11.58\text{\AA}$  and  $c = 26.33\text{\AA}$  is proposed by Yakel, Pauling & Corey (58), and the  $\alpha$ -helix is strongly supported by the diffraction pattern. Positions for the  $\beta$  carbon atoms are suggested. An interpretation of the infrared dichroism in poly- $\gamma$ -benzyl-L-glutamate by Frazer & Price (59) supported the  $\alpha$ -helix as the correct configuration, in disagreement with the earlier work of this type by Bamford *et al.* (60). Pauling & Corey (47) showed that the Fourier transform of the  $\alpha$ -helix showed good correspondence with the diffraction pattern of the equatorial reflections from poly-N-methyl-L-glutamate. A note by Cochrane & Crick (61), and a fuller description by these authors and Vand (62) show that this correspondence exists over the whole diffraction pattern. This discovery and establishment of the  $\alpha$ -helix, or some helix very nearly identical with it, has been one of the major advances in the structure of polypeptides and proteins.

There is good evidence, discussed by Perutz (49), for the occurrence of the  $\alpha$ -helix in other proteins. It seems to be relatively certain that the controversial Lotmar-Picken x-ray pattern of dried muscle is consistent with the  $\alpha$ -helix (63) in spite of contrary claims (64). This controversy is in part evidence of the effect of the comparatively recent very precise proposals of protein structures on the reevaluation of existing experimental data, and on the care with which new data must now be taken.

Additional structures for polypeptide chains have also appeared during 1952. Pauling & Corey (65) have described a number of new structures all containing equivalent *cis* amide groups. Other proteins have also been discussed. The orientation of polypeptide chains in insulin acid sulfate has been described by Low (66) to be along the  $a$  ( $44\text{\AA}$ ) axis of the orthorhombic unit cell containing four molecules of molecular weight 12,000. Each molecule has four chains linked by disulfide groups. Three papers have appeared on haemoglobin structures, discussion of which is covered in the review by Perutz (49) to which the reader is referred.

#### INORGANIC CRYSTALS AND INTERMETALLIC COMPOUNDS

In view of the emphasis of the previous reviews on inorganic structures, only selected papers and related topics are discussed, even though the number of inorganic crystallographic studies has, as usual, far exceeded those of organic compounds.

The structures of elements received some attention in 1952. The structure of solid  $\text{Cl}_2$ , determined by Collin (67), is very similar to that of  $\text{Br}_2$  and  $\text{I}_2$ ; the structure previously proposed by Keesom & Taconis (68) is incorrect. All of these halogens have abnormally short intermolecular interactions, which for  $\text{Cl}_2$  are at a distance of  $3.34 \text{ \AA}$ ,  $0.26 \text{ \AA}$  less than the usual van der Waals distance. In  $\text{I}_2$ , where this interaction is  $0.76 \text{ \AA}$  shorter than the van der Waals distance of  $4.30 \text{ \AA}$ , a study of the quadrupole coupling (Townes & Dailey, (69) indicates about 9 per cent of a covalent bond in this  $3.54 \text{ \AA}$  distance, a value which incidentally is almost three times the percentage covalent contribution calculated from Pauling's rule,  $d = d_1 - 0.6 \log n$ . Of course, this rule was derived for the larger bond orders, and it is not surprising that modification for small  $n$  is necessary. The structure of  $\beta$ -monoclinic selenium, determined by Burbank (70), consists of an eight-membered chain very similar to the eight-membered puckered ring in  $\alpha$ -monoclinic selenium [Burbank (71)] but with one Se—Se bond opened up. This structure for  $\beta$ -monoclinic selenium has been shown to be incorrect by Marsh, McCullough & Pauling (72), who find the same puckered eight-membered ring that occurs in the  $\alpha$ -monoclinic form. A puckered eight-membered ring also occurs in realgar,  $\text{As}_4\text{S}_4$ , the structure of which has been determined in the solid state by Ito, Morimoto & Sadanaga (73). The structure of  $\text{S}_4\text{N}_4$  determined in the solid state by Clark (74) has also a puckered eight-membered ring but with an anomalous cross ring S—S distance of only  $2.58 \text{ \AA}$ . Both of these studies confirm the molecular structures determined previously by Lu & Donohue (75) by the electron diffraction method.

The controversies over the  $\beta$ -uranium and closely related  $\sigma$ -phase, continue (76 to 81). However, the conclusions presented by Zachariasen in the review of last year appear to be correct and are confirmed by the additional studies of the year 1952.

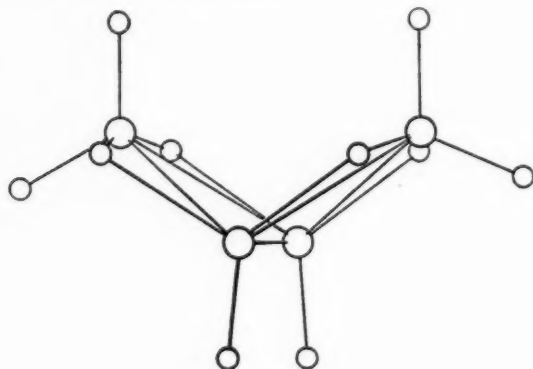
The  $\text{MX}_{12}$  and  $\text{MX}_{13}$  phases of intermetallic compounds received some attention. The structure of  $\text{TiBe}_{12}$  determined by Raeuchle & Rundle (82) has an unusual disorder and an unusual set of absences. The structure of  $\text{ThMn}_{12}$ , and other phases in this system, have been shown by Florio, Rundle & Snow (83) to be similar but not identical with the corresponding Fe, Co, and Ni compounds. The structures of  $\text{MBe}_{13}$  where M is U, Th, Ce, or Zr have been shown by Koehler, Singer & Coffinberry (84) to support the cubic structure proposed by Ketelaar (85) and by Zintl & Hauke (86) in 1937; the  $\text{UBe}_{13}$  compound was studied by neutron diffraction. A refinement of the parameters in  $\text{NaZn}_{13}$  and a discussion of valence, electron transfer, and Brillouin zones has been published by Shoemaker *et al.* (87).

The structures of a number of interesting boron compounds have been studied, and it may be hoped that further studies will yield information with respect to directed valence on this border-line between metals and non-metals. The structure of  $\text{B}_2\text{O}_3$ , described by Berger (88), contains boron in tetrahedral coordination, but not all of the B—O bond distances are the same. Crystals of  $\text{Mg}_2\text{B}_3\text{O}_8$  contain the "double triangle"  $\text{B}_2\text{O}_5^{4-}$  groups

according to Takeuchi (89). It is interesting that the monoclinic form of metaboric acid,  $\text{HBO}_2$ , contains both  $\text{BO}_4$  tetrahedra and  $\text{B}_2\text{O}_5$  groups linked to form infinite chains [Zachariasen (1)]. These chains are then linked to one another by hydrogen bonds.

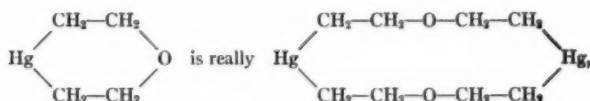
Boron nitride, BN, has layers like those of graphite with alternating B and N in the hexagons. However, the stacking of these layers has been shown by Pease (90) to be different from that in graphite. In BN, the hexagons are packed directly above one another, but with B above N and N above B, so that alternate layers constitute the true repeat. Analogies and differences with corresponding carbon compounds are also discussed by Coursen & Hoard (91) who have made a very precise study of B-trichloroborazole. The B—Cl bond is  $1.76\text{\AA}$  and the BN bond is  $1.41\text{\AA}$  in length. A further discussion of the bonding in this compound is given by Pease (92). The band structures, with particular reference to the  $\pi$ -states have been discussed and compared in graphite and boron nitride [Coulson & Taylor (93); Duncanson & Coulson (94); Taylor & Coulson (95)].

A correlation of known structures of the simpler electron deficient compounds of boron has been made by Hedberg (96), who achieved a systematic discussion of bond distances on the assumptions of a boron radius of  $0.80\text{\AA}$  and of Pauling's rule for bond order,  $d = d_1 - 0.6 \log n$ . The correlation includes the recently published full account of the tetragonal pyramidal ( $C_{4v}$ ) structure of  $\text{B}_5\text{H}_9$  by Dulmage & Lipscomb (97) and by Hedberg, Jones & Shomaker (98). The structure of the newly discovered compound  $\text{B}_4\text{Cl}_4$  also is consistent with the scheme of radii; this molecule contains very nearly a regular tetrahedron of boron atoms with an average B—B distance of  $1.70\text{\AA}$ , and with one chlorine atom singly bonded to each boron atom at a distance of  $1.70\text{\AA}$  in a direction away from the center of the tetrahedron [Atoji & Lipscomb (99)]. The structure of  $\text{B}_4\text{H}_{10}$ , however, contains an opened tetrahedron, with one B—B bond about  $2.8\text{\AA}$  in length [Nordman & Lipscomb (100); Jones, Hedberg & Schomaker (101)] and with all other B—B distances between  $1.7$  and  $1.9\text{\AA}$ :



Although Pauling's rule provides a basis for understanding the bond distances once the molecular structures are known, there seem to be too many ways of obtaining predicted structures with the use of this rule alone. Aside from the fact that boron arrangements are based on the icosahedron, the octahedron, the tetrahedron, or fragments of these polyhedra, and the fact that boron triangles tend to predominate, it is not yet clear what principles govern the bond angles in these and related electron deficient compounds of boron. The answers may be forthcoming from a systematic study of these and other boron compounds.

Compounds containing unusual molecules and complex ions have been studied.  $\text{PbCl}_4\text{I}$  is shown by Zelenzny & Baenziger (102) to consist of  $\text{PbCl}_4^+$  tetrahedra and linear  $\text{Cl}-\text{I}-\text{Cl}^-$  ions. The structure of paratungstate ion  $\text{W}_{12}\text{O}_{46}^{2-}$  has been elucidated by Lindqvist (103). Two salts of the  $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$  ion have been studied by van Niekirk & Schoening (104). The chemically reasonable structure of the  $\text{S}_2\text{O}_5^{2-}$  ion has been confirmed by Taylor & Beevers (105) showing, as expected, a central sulfur atom bonded to three oxygens at a distance of  $1.5 \text{ \AA}$  and one sulfur at a distance of  $2.0 \text{ \AA}$ . A thorough study of the structure of the compound usually written as  $\text{N}_2\text{O}_5 \cdot 3\text{SO}_3$  has been shown by Eriks & MacGillavry (106) to be  $(\text{NO}_2^+)_2(\text{S}_3\text{O}_{10}^{2-})$ , in which the nitronium ion is linear and the sulfurs are linked through oxygen atoms in the  $\text{S}_3\text{O}_{10}^{2-}$  ion. The polyatomic interhalogen compounds continue to show very surprising structures: Burbank (107) has shown that  $\text{ClF}_3$  is a planar T shaped molecule with Cl approximately at the center and top of the T. His study formed the starting point of a microwave study by Smith (108), who found two Cl-F distances at  $1.70 \text{ \AA}$  and one Cl-F distance at  $1.56 \text{ \AA}$ . The tetrahedral coordination of paramagnetic nickel II is indicated for the salicylaldehyde salt by the similarity of the diffraction pattern to the Zn II salt, unlike that of the presumably planar Cu II salt [Curtiss, Lyle & Lingafelter (109)]. The structure usually written as



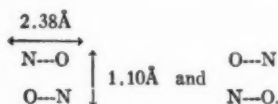
as has been shown by Grdenic (110).

The hydrates of rare gases and simple organic and inorganic molecules have been studied by Pauling & Marsh (111), von Stackelberg & Müller (112, 113), and Claussen (114). There are two types of structures. One is cubic with  $a=12 \text{ \AA}$  containing 46 water molecules, 2 small holes and 6 medium sized holes, thus giving rise to  $5\frac{1}{4} \text{ H}_2\text{O}$  molecules or  $7\frac{1}{2} \text{ H}_2\text{O}$  molecules per trapped molecule. The other structure is also cubic with  $a=17.2 \text{ \AA}$ , containing 136 water molecules, 8 large holes and 16 smaller holes and thus giving rise to hydrates such as  $\text{CHCl}_3 \cdot 2\text{H}_2\text{S} \cdot 17\text{H}_2\text{O}$ , etc.

A number of problems involving various aspects of hydrogen bonding have been studied. A review of hydrogen bonds of interest in relation to



amino acids and related compounds, written by Donohue (115), indicates how one may locate hydrogens indirectly, and how one may reach important conclusions about molecular structures especially when hydrogen tautomerism causes ambiguities in the formulation of molecular structures. In another study by Nordman & Lipscomb (116) the effects on the bond length of the substitution of hydrogen by deuterium has received a theoretical interpretation based on the mean amplitudes of vibration, and on the shapes of the various expected potential functions. Most hydrogen bonds are unsymmetrical. However, Rundle & Parasol (117) have shown that a double minimum probably does not occur in the shortest O . . . O hydrogen bonds, and a neutron diffraction study of  $\text{KHF}_2$  by Peterson & Levy (118) shows that the equilibrium position of the hydrogen atom in the anomalously short  $\text{HF}_2^-$  ion is halfway, at least within  $0.1\text{\AA}$ , in agreement with the conclusions based on the residual entropy study of Westrum & Pitzer (119). A study of the effects of hydrogen bonding on the residual entropy of methanol has been published by Tauer & Lipscomb (120), who also made a detailed study of the phase transition. In agreement with the tentative conclusion of the thermodynamic study by Weltner & Pitzer (121), the residual entropy is zero. The residual entropy of the dimer of nitric oxide has been satisfactorily explained on a structural basis by Dulmage, Meyers & Lipscomb (122) in terms of the two possible orientations of the rectangular planar dimer,



The very unusual weak bond may be a sort of "outer complex" of the type described by Mulliken (40), while the short bond is of a length intermediate between the double and triple bond lengths. It is worth recalling that an unusually long N . . . N bond, of length  $1.64\text{\AA}$ , was found by Robertson & Broadley (123) in the dimer of  $\text{NO}_2$ . One of the most important of the remaining residual entropy problems is that of phosgene. The structure of the solid, determined by Zaslow, Atoji & Lipscomb (124) shows that the residual entropy is zero, but the calorimetric study by Giauque & Jones (125) indicated a residual entropy of 1.63 e.u. Certainly the type of disorder suggested in the calorimetric study did not exist in the crystals studied by x-ray diffraction. Probably the difficulty lies in the vibrational assignment.

Further studies of many other types of disorder were published during 1952, but only a brief mention of a few specific results can be made. That the transition in  $\text{NH}_4\text{Cl}$  involved orientational disorder to order as the temperature is lowered was proved in a neutron diffraction study by Levy & Peterson (126), thus clarifying an existing discrepancy with the interpretation of heat capacities and spectra. A number of studies of the types of order-disorder transitions that are responsible for ferroelectric properties of

both the acid phosphate type and the barium titanate type of ferroelectrics have been published, but these seem to be more properly the subject of a review sufficiently extensive to do justice to the topic. Finally, an unusual type of ferromagnetic crystal, with the composition  $\text{BaFe}_{18}\text{O}_{27}$ , has been described by Wijn (127) and Braun (128).

An additional five new types of silicon carbide have been described by Ramsdell & Kohn (129) who propose a cluster-type of theory for the formation of the many polymorphs, now amounting to 14 fully-described types. Structures of two of these types have also been elucidated by Glasilova, Beletskii & Sokhor (130) and by Glasilova & Sokhor (131), and an investigation of the effect of disorder on the diffraction patterns of some of the more usual structure types has been made by Gevers (132).

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# REACTION KINETICS<sup>1</sup>

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## CHEMICAL KINETICS

It is not possible within the space limitations of this chapter to make a thorough review of all areas in chemical kinetics, nor to be complete within each area. Among the phases which have been covered fairly thoroughly are oxidation-reduction reactions, and the kinetics of substitution at metal ion centers. This emphasis came naturally since the reviewer has had a continuing interest in these fields, but it was admitted only because a rapid growth of activity in them seems certain. Other fields which seem likely to invite increased attention are: elementary free radical reactions, induction periods, phenomena in shock waves, and rates in nonpolar solvents. The important field of kinetics of enzyme reactions has been omitted entirely. It is hoped that the hiatus will help stimulate a succeeding reviewer to do a thorough job in this interesting field.

## GENERAL THEORETICAL PAPERS

Several papers have dealt with the theory of the decomposition of activated complexes. Benson (1) has continued the application and extension of Slater's (2) treatment of the adiabatic decomposition of unstable molecules, discussing bimolecular as well as unimolecular processes, and applying the equations developed to the pressure dependence of the first-order specific rate in unimolecular reactions, and to the recombination of atoms and radicals. Marcus (3) has offered a more general derivation of the equations of Marcus & Rice (4) describing unimolecular decomposition, and has applied (5) the treatment to the decomposition of activated complexes resulting from the recombination of free radicals. Johnston (6), analyzing the generalized Lindeman mechanism for unimolecular reactions, has defined the relation of the rate characteristics in the high concentration region to those of the low concentration region.

The kinetic properties of systems involving consecutive reactions have received considerable attention. Benson (7) has discussed induction periods in such systems, Skrabal (8), the theory of periodic reactions, Hinshelwood (9) the kinetics of autolytic systems, Natta & Mantica (10) the distribution of products in consecutive competitive reactions, and Frost & Schwemer (11) have described a method for evaluating rate constants from data for competitive consecutive second-order reactions. Skrabal (12) has defined the concept of independent reactions, given it a mathematical formulation and shown how it applies to the kinetics of complex systems.

<sup>1</sup> The survey of the literature pertaining to this review was completed in November, 1952.

A third aspect of the theory of rate processes is the correlation of reactivity with properties of the reactant species. Smith & Eyring (13, 14) applied a method previously described (15) of calculating the charge distribution in organic molecules in explaining the relative rates of reaction of sodium with alkali halides, and of atomic chlorine with hydrocarbons. Gilchrist & Sutton (16) have discussed the relation of bond length to reactivity. The papers by Jaffe (17) using molecular orbital theory to calculate  $\sigma$  values, and of Roberts & Streitwieser (18) on the calculation of orientation effects in aromatic molecules also belong in this general area.

Rollefson (19) has directed attention to the range covered by the geometrical requirements of the activated complex in bimolecular reactions. In one extreme, a bond between the reactants is required, and because of the large entropy decrease (translational) accompanying such an association, these reactions will have as "normal" frequency factors rather low values,  $\sim 10^7$  l. mole<sup>-1</sup>min.<sup>-1</sup>. In the other extreme, the only requirement is that the reacting partners approach within a certain radius, and for these processes the "normal" frequency factors will be *ca.*  $10^4$  greater.

#### GAS PHASE REACTIONS

*Reactions involving ions.*—An interesting class of elementary gas phase reactions involves ions. Several papers in this field, concerned with electron transfer in the gas phase will be mentioned. Their intrinsic interest is great and is enhanced by the relation they have to electron transfer reactions in solution. This relation was implied by including papers dealing with both types of reactions in a symposium held at the University of Notre Dame in June, 1952, and is developed in some detail in a paper by Libby (20) given at the symposium. Hornbeck (21) reviewed the data on electron transfers between inert gas atoms and the corresponding monovalent ions, as determined by measuring the mobilities of the ions in the parent gas. Electron transfer provides a mechanism for momentum transfer, thus affecting the mobility, and for the gases Ne, He and Ar is observed to have a cross-section three to four times that measured by gas viscosities. Muschlitz & Simons (22) described the method they have used in measuring the efficiency of electron transfer between protons and various types of molecules. The electron transfer process produces slow ions, and this characteristic is exploited in determining their number. The paper included a review of data which have been obtained using 100 e.v. protons. For the series of inert gas atoms, the efficiency reaches a maximum at Kr corresponding to the smallest difference between the ionizing potential of H and of the inert gas atom. The relations for complex hydrocarbon molecules are not simple to summarize. As was pointed out by Davidson (23) in the discussion of these papers, the Franck-Condon Principle imposes an additional requirement when at least one of the partners has vibrational degrees of freedom.

*Elementary free radical reactions.*—Work on the specific rate of the association reaction:



1.

has continued, and has confirmed the value earlier arrived at by Gomer & Kistiakowsky (24). The low value  $4.4 \times 10^{-6}$  of the collision efficiency reported by Miller & Steacie (25) depended on the collision efficiency of the reaction of NO and  $\text{CH}_3$ . A reinvestigation of the latter reaction by Durham & Steacie (26) led to a revision of its collision efficiency upward by a factor of about 10 to  $1.5 \times 10^{-4}$ . This revised value yields 0.01 as a lower limit of the collision efficiency of reaction 1. Further confirmation of a value close to unity for the efficiency of recombination of methyl radicals derives from a mass-spectrometric measurement of methyl radical concentrations in systems in which di-*t*-butyl peroxide and mercury dimethyl were decomposed thermally. Applying this technique, Lossing & Tickner (27) arrived at 0.02 as the collision efficiency of reaction 1 considering this value accurate within a factor of three.

The determination of the recombination rate of methyl radicals is a great step forward in gas phase reaction kinetics, since it is then possible from competition studies to determine the specific rate of reaction of methyl radicals with other molecules. The review of work of this type which follows, includes only systems in which radicals are generated by thermally induced reactions. Volman & Brinton (28) measured the relative amounts of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  produced on the pyrolysis of a mixture of acetaldehyde and di-*t*-butyl peroxide. Their data covering a 17-fold range in acetaldehyde pressure is consistent with the mechanism:



The ratio  $k_2/\sqrt{k_1}$  obtained from their data, when combined with the accepted value for  $k_1$ , yields for  $k_2$  over the temperature range  $124^\circ$  to  $156^\circ\text{C}$ . the expression  $4.2 \times 10^{10} \sqrt{T} e^{-7,600/RT}$  cc. mole $^{-1}$  sec. $^{-1}$ . The activation energy for reaction 2 thus measured is lower than that obtained in photochemical studies. It is a plausible value, however, since it brings the steric factor for reaction 2 ( $3.7 \times 10^{-3}$  assuming a collision diameter of  $3.7\text{\AA}$ ) into line with others observed for hydrogen abstraction reactions of methyl radicals. In a similar analysis of a system involving the pyrolysis of a mixture of acetone and di-*t*-butyl peroxide Jaquiss, Roberts & Szwarc (29) measured 9.5 kcal. for  $E_4 - 1/2 E_1$  (reaction 4 is:  $\text{CH}_3 + \text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_4 + \text{CH}_2\text{COCH}_3$ ). This figure agrees with a recent value derived from photochemical studies [9.5 kcal., Raal & Steacie] (30), as well as with the older photochemical value of 9.7 kcal. The excellent agreement obtained using such distinctly different systems is good evidence that an intermediate common to both is being studied, and qualifies both as sources of methyl radicals. Brinton & Volman (31) report for the specific rate of reaction of methyl radicals with ethyleneimine:  $4.5 \times 10^{10} e^{-4,800/RT}$  cc. mole $^{-1}$  sec. $^{-1}$ .



In a review of the reactions of ethyl radicals Ivin, Wijnen & Steacie (32) note that the recombination, in common with that of methyl radicals, proceeds with a high efficiency, of the order of 0.1. The disproportionation to ethane and ethylene is a competing reaction, which also has a low activation energy, perhaps 0.8 kcal. greater than the association. The steric factors for hydrogen extraction reactions are of the order of  $10^{-3}$  to  $10^{-4}$ .

The direct reaction of atomic hydrogen with  $C_2H_4$  has been studied by Berlie & LeRoy (33) using a method described by Dingle & LeRoy (34). The activation energy, based on a temperature variation from  $80^\circ$  to  $163^\circ C$ . is reported as  $6.2 \pm 0.1$  kcal., and the steric factor calculated using  $2.9 \text{ \AA}$  as the collision diameter, as  $3.3 \times 10^{-3}$ .

Bywater & Roberts (35) have made a straightforward calculation of the steric factors in hydrogen abstraction reactions of  $CH_3$  and H. The authors assumed a collinear arrangement of the atoms directly concerned. The methyl radical was assumed planar, with C—H distance at  $1.11 \text{ \AA}$ , and was assumed to retain one degree of rotational freedom in the activated complex. The agreement with experimental values (which include reactions of H with  $H_2$  and with  $C_2H_6$ , and of  $CH_3$  with  $H_2$ ,  $C_2H_4$  and *iso*-butane) is satisfactory. The major contribution to the entropy of activation is the loss of translational entropy, which in the case of a light molecule attacking a massive one, comprises the total translational entropy of the light partner. Considering this factor for  $CH_3$ , and the additional one that in the limiting case of a massive co-reactant, 4 e.u. of internal rotation replaces 10.7 e.u. of free rotational entropy the minimum temperature independent factor is calculated as  $6 \times 10^9$  cc. mole $^{-1}$  sec. $^{-1}$ .

Studying the competition between the decomposition of  $(CH_3)_3CO$  and its reaction with ethyleneimine and making the assumption that the activation energy for the latter reaction is the same as that of  $CH_3$  with the same substrate, Brinton & Volman (31) arrived at  $17 \pm 2$  as the activation energy for the decomposition of  $(CH_3)_3CO$ .

*Results relating to the theory of unimolecular processes.*—Pritchard, Sowden & Trotman-Dickenson (36) have extended measurements on the transformation of cyclopropane to propylene to pressures one-tenth of those reached in earlier work (37). The theoretical curve of Chambers & Kistiakowsky (37) (collision diameter,  $3.9 \text{ \AA}$ , 13 oscillators, and  $\log k_\infty$  (sec. $^{-1}$ ) =  $15.17 - 65,000/2.3RT$ ) fits the data to the lowest pressures. The conclusion stated by Corner & Pease (38) that the falling off in specific rate at low pressures is a consequence of a complex reaction mechanism is set aside by the new work in which it was shown that  $H_2$  does restore the specific rate, although its efficiency for this purpose is only  $\frac{1}{3}$  that of the reactant or product molecules. Howlett (39) has outlined evidence that the chloroethane, 1:1-dichloroethane and isopropyl chloride decompose, in pyrolysis, by unimolecular mechanisms. The kinetic behavior is strikingly different from that of another class, including, for example, *sym*-dichloroethane, which is known to decompose by chain reactions. No induction periods are observed, and the rates are insensitive to reagents such as  $O_2$ ,  $Cl_2$  and propylene known to react with radicals of the

kind which would be in question. This evidence was amplified by new work in which for each of the first group, the specific rate was observed to fall off at low pressure. For  $\text{CH}_3\text{CHCl}_2$ , in fact, the second-order rate region was entered at 0.1–1 mm. pressure. In each system, HCl restores the low specific rates to the limiting high pressure values, but does not affect the rate in the high pressure region. The data for  $\text{CH}_3\text{CHCl}_2$  were sufficiently complete to respond to a detailed treatment. There was found to be a marked curvature in the plot of  $1/k$  versus  $1/P$ , showing that a localized energy treatment is necessary to explain the data (40).

*Rapid gas phase reactions.*—Freiling, Johnston & Ogg (41) studied the reaction:



using the absorptiometric technique developed by Johnston & Yost (42). The reaction was found to be first order in each reactant over a pressure range 10 fold in each and is apparently homogeneous. The specific rate in this temperature range 27° to 71°C. was found to be:  $6.83 \times 10^{12} e^{-6,900/RT}$  cc. mole<sup>-1</sup> sec.<sup>-1</sup>.





Further applications of the flame technique have been described. Cvetanovic & LeRoy (43) followed their examination of the theory of the method with a careful investigation of the reaction  $\text{Na} + \text{C}_2\text{H}_5\text{Cl}$  (44). They studied the rate as a function of temperature (260° to 380°C.) and applied the results of their extended theory in correcting the specific rates calculated from the Hartel-Polanyi approximation. The activation energy was measured as  $10.2 \pm 0.5$  kcal. per mole. Using for the square of the collision diameter  $\sigma$  a value  $3.5 \times 10^{-16}$  cm.<sup>2</sup>, the steric factor  $p$  was calculated to be 1.0–0.3. Thus, the assumption, commonly made in the absence of data at a variety of temperatures, that the product  $p\sigma^2$  is in the neighborhood of  $3.5 \times 10^{-16}$  cm.<sup>2</sup>, is confirmed at least for the present system. Hodgins & Haines (45) studied the reaction of Na with  $\text{CF}_3\text{I}$ ,  $\text{CF}_3\text{Br}$  and  $\text{CF}_3\text{Cl}$ . With  $\text{CF}_3\text{Cl}$  the activation energy was found as 7.0 kcal., and  $p\sigma^2$  as  $3.5 \times 10^{-16}$  cm.<sup>2</sup>. The values of  $E$  for  $\text{CF}_3\text{Br}$  and  $\text{CF}_3\text{I}$  are calculated as 2.3 and 1.8 kcal. when this value of  $p\sigma^2$  is retained. The range of systems amenable to analysis by the flame technique was greatly extended by Garvin & Kistiakowsky (46). In a study of the association of  $\text{BF}_3$  with methyl amines, they outlined the reaction gradient by measuring the temperature throughout the reaction zone with a thermocouple. The temperature change was small enough so that the heat of reaction, specific rate and diffusion coefficients were essentially constant. The activation energies of the association reactions were found to be zero. At the pressures prevailing, dissociation of the activated molecules formed on association competed with deactivation by collision. The specific rates for  $\text{MeNH}_2$ ,  $\text{Me}_2\text{NH}$  and  $\text{Me}_3\text{N}$  (in cc. mol.<sup>-1</sup> sec.<sup>-1</sup>) were reported as  $10^{13}$  divided by  $(1+1.16/P)$ ,  $(0.31+0.444/P)$  and  $(2.68+0.041/P)$  respectively, with  $P$ , the total pressure expressed in mm.

*Single substance reactions; isomerizations, decompositions.*—Two first order reactions in this category have been described with appear to be relatively clean and homogeneous and are probably unimolecular. Rabinovitch,

Douglas & Looney (47) have studied the *cis-trans* isomerization of di-deuteroethylene in quartz over a pressure range 9–310 mm. and a temperature range of 450°–550°C. The reaction rate is independent of the surface to volume ratio. The *A* factor was observed to be  $3 \times 10^{12}$  sec.<sup>-1</sup> and the activation energy  $61.3 \pm 1.2$ . The result is of special interest since the reaction apparently proceeds through a singlet excited state, and thus the activation energy measures the energy required to form the lowest singlet state of perpendicular C<sub>2</sub>H<sub>4</sub>. The decomposition rates of (–)-menthyl chloride were observed by Barton, Head & Williams (48) to settle down to stable reproducible values on repeated use of the glass reaction vessels, independent of surface to volume area. There was no induction period and no effect of propylene on the rates. The total rate as function of temperature is given by  $10^{12.6} e^{-45,000/RT}$  sec.<sup>-1</sup>. The two isomers formed on elimination of hydrogen chloride appear at fairly constant ratio over the whole range of temperatures.

The method of quenching free radicals by added reagents, and thereby controlling pyrolytic processes has been applied with continued success by Szwarc and co-workers (49–54). A summary of the new results appears in the following table:

TABLE I  
DATA ON THE FORMATION OF RADICALS BY PYROLYSIS

Process	Temp. Range °K	<i>A</i> , Sec. <sup>-1</sup>	<i>E</i> kcal.	–Δ <i>H</i> <sub>f</sub> <sup>*</sup> kcal.	Ref.
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ... C <sub>2</sub> H <sub>5</sub>	887–1036	$3 \times 10^{12}$	57.5	22 ± 4	(49)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ... C <sub>3</sub> H <sub>7</sub>	879– 974	$3 \times 10^{14}$	65.0	22 ± 4	(50)
CH <sub>3</sub> ... HCCCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	906–1001	$2 \times 10^{13}$	61.0	30	(51)
CH <sub>3</sub> ... HCCCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	897– 961	$2 \times 10^{13}$	60.0	21	(51)
CH <sub>3</sub> ... C(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	937– 979	$3 \times 10^{13}$	59.5	22	(51)
Br ... C <sub>6</sub> H <sub>5</sub>	1030–1143	$2 \times 10^{13}$	70.9	69.6 ± 3	(52)
Br ... COC <sub>6</sub> H <sub>5</sub>	—	—	57.0 ± 1	15.6 ± 1	(53)
 ... Br	1022–1133	$1.5 \times 10^{13}$	70.0	—	(54)
 ... Br	1014–1133	$3.5 \times 10^{13}$	70.9	—	(54)
 ... Br	1002–1125	$1 \times 10^{13}$	67.7	—	(54)
 ... Br	964–1062	$1.5 \times 10^{13}$	65.6	—	(54)
C <sub>2</sub> H <sub>5</sub> O ... OC <sub>2</sub> H <sub>5</sub>	483– 518	$2 \times 10^{13}$	31.7	8.1	(55)

\* Refers in each case to the standard heat of formation of the radical on the right in Column 1.

The evidence from stoichiometry is that under the conditions of the experiments,  $C_2H_6$  decomposes to  $C_2H_4 + H$ ,  $C_2H_7$  to  $CH_3 + C_2H_4$ , and the radicals derived from cumene, *p*-cymene and *t*-butyl benzene decompose to olefin and  $H$ , more rapidly than the intact radicals react with toluene. In the decomposition of diethyl peroxide [Rebert & Laidler (55)] the indications are that following the  $O-O$  bond rupture the reactions:  $C_2H_5O \rightarrow CH_3 + CH_2O$ ,  $2CH_3 \rightarrow C_2H_6$  and  $CH_3 + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2$  take place.

Blades & Murphy (56) also used the Szwarc method in a study of the decomposition of vinyl ethyl ether. The products are largely  $CH_3CHO$  and  $C_2H_4$  and may arise as such in the primary process, the carrier gas in this system serving only in eliminating the effects of a minor free-radical path. The reaction is first order in the ether, and the specific rate function is:  $2.7 \times 10^{11} e^{-43,800/RT}$  sec.<sup>-1</sup>. The authors consider the entropy of activation,  $-7.7$  e.u. at  $170^\circ$ , to be in harmony with a cyclic intermediate, including in the ring the carbon-oxygen skeleton and a hydrogen atom transferred from the ethyl to the vinyl group. The same entropy of activation was observed by Stein & Murphy (57) in the rearrangement of isopropenyl allyl ether to allyl acetone. This is also a first order reaction, apparently homogeneous. The specific rate is reported as  $5.4 \times 10^{11} e^{-29300/RT}$  sec.<sup>-1</sup>.

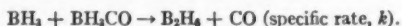
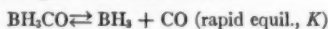
In a paper by Peard, Stubbs & Hinshelwood (58) previous work [Stubbs *et al.* (59), Peard, Stubbs & Hinshelwood (60)] on the decomposition of aliphatic hydrocarbons in the presence of  $NO$  as radical suppressor is summarized. Ethane, propane, *iso*-butane, *iso*-pentane, *neo*-pentane, and *neo*-hexane show "normal" behavior. The limiting rate at high inhibitor concentration is first order in the reactant hydrocarbon, and the specific rate decreases at sufficiently low pressure, as expected for a unimolecular reaction. The activation energy is independent of pressure over wide limits. For another class, including the straight chain hydrocarbons from butane to heptane, as well as some branched chain compounds, the first order specific rate as function of pressure, after passing through a transition of the type described above, levels off, then falls again at still lower pressure. The activation energy in the transition region is pressure dependent, and in fact, in the lower pressure region depends on the nature of the gas present.

The pyrolysis of 1:2-dichloroethane described by Howlett (61) has interesting kinetic features. The first order specific rate falls at low pressures and is restored by  $HCl$ . However, the reaction is not a simple unimolecular process, as shown by the existence of an induction period, and the inhibitory effect of propylene. Howlett proved the use of a thorough study of the induction period in determining functions of the specific rate different from those given by steady-state measurements. On the basis of his results, Howlett suggested a complete mechanism in which some relations between the specific rates were established, and reasonable assignments of activation energies for all the steps made. Howlett (62) has also discussed the induction period in the decomposition of  $C_2H_6$ , using as a basis the Rice-Herzfeld mechanism, and concluding that the induction period should be measurable, of the order of 27 sec. at  $850^\circ K$ . Boyer, Niclaue & Letort (63) have published new data

on the chain decomposition of acetaldehyde, as a spontaneous reaction, and as catalysed by *di-t*-butyl peroxide and by diacetyl. Effects due to the changes in the surface/volume ratio were only slight. It seems likely from this and from the kinetic evidence that the reactions were essentially homogeneous. The rate laws observed were:  $-d(\text{acet.})/dt$  in  $l^{1/2}$  mole $^{-1/2}$  min. $^{-1}$   $= 0.4 \times 10^{13}$  (acet.) $^{3/2} e^{-48,000/RT}$  (spontaneous);  $= 1.25 \times 10^{13}$  (perox.) $^{1/2}$  (acet.) $^{0.9} e^{-26,000/RT}$  (catalysed by *di-t*-butyl peroxide);  $5.25 \times 10^{15}$  (diac.) $^{1/2}$  (acet.)  $e^{-51,500/RT}$  (catalysed by diacetyl). The activation energy observed for catalysis by peroxide is just what would be expected for a process having rupture of the peroxide ( $\frac{1}{2}D = 19$  kcal.) as the chain initiating step, recombination of methyl radicals as chain breaking step, and  $\text{CH}_3 + \text{CH}_3\text{CHO}$  ( $E = 7.5$  kcal., Ref. 28) as the rate determining chain carrying step. The intimate relation of the spontaneous change to the catalysed change is shown by the relation established:  $v = v_1^2 + v_2^2$ , where  $v$  is the over-all rate, and  $v_1$  and  $v_2$  are the individual velocities of the contributing reactions, under the same conditions. The kinetic observations (64) on the decomposition of propionaldehyde catalysed by diacetyl are similar to those for acetaldehyde.

Molera & Stubbs (65) made observations on the decomposition of seven olefins, using a static system with pressure change as index of reaction rate, but including complete analysis in some cases. The rates, initial and also after considerable progress of reaction, are first order in olefin. The activation energies reported are: butene-1, 66 kcal., butene-3, 56, iso-butene, 54, 2 methyl butene-1, 62, 3 methylbutene-1, 63, hexene-1, 53, heptene-1, 49.

There have been a few studies of the decomposition of inorganic compounds. Wise & Frech (66) observed that the activation energy for the decomposition of NO changes from 21.4 kcal. at the low temperature region, to 78.2 kcal. at the upper, over the range 872° to 1275°K, although the reaction is second order throughout. At lower temperatures, but not at the upper,  $\text{N}_2$  accelerates the reaction, and presumably the mechanism changes from a heterogeneous to a homogeneous one. Oxygen accelerates the reaction over the whole range, and its effect is expressible by adding the term:  $k(\text{NO})(\text{O}_2)^{3/2} / (\text{NO}) + a(\text{O}_2)$  to the rate law. Fenimore & Kelso (67) have published some observations on the decomposition of NO catalysed by  $\text{NH}_3$ . Brokaw & Pease (68) note that the rate of decomposition of  $\text{Al}(\text{BH}_4)_3$  to  $\text{H}_2$  and solid products is independent of the surface area, and of the accumulation of solid. The kinetic behavior of the system follows that of successive first order reactions with reversible steps. Burg (69) has studied the equilibrium and kinetic properties of the system:  $2\text{BH}_3\text{CO} = \text{B}_2\text{H}_6 + 2\text{CO}$ . The observations on the kinetics, except for a slight indication of a heterogeneous path correspond to the homogeneous mechanism:



The product  $kK$  is given by:  $1 \times 10^{14} e^{-27,500/RT}$  sec. $^{-1}$ .

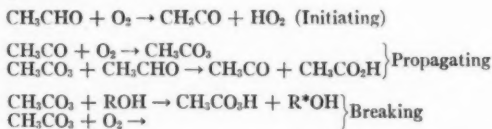
*Reactions of mixtures of substances.*—The dimerizations and associations of some fluoroethylenes are second order processes, and are apparently homogeneous and uncomplicated [Lacher, Tompkin & Park (70)]. The activation energies for each of the processes  $2C_2F_4 + C_2F_3Cl$  and  $2C_2F_3Cl$  were found to be 26.3 kcal., and  $A$  factors  $16.5 \times 10^{10} + 8.5 \times 10^{10}$  and  $3.5 \times 10^{10}$  cc. mole<sup>-1</sup> sec.<sup>-1</sup> respectively. Noting that the chief contribution to the differences in entropies of activation will be determined by the symmetry numbers, the authors conclude that the data favor a puckered rather than a planar ring in the activated complex. For the homogeneous second-order reaction of  $C_2N_2$  with butadiene, Hawkins & Janz (71) found the activation energy to be 31.6 kcal. and the  $A$  factor  $16 \times 10^{12}$  cc. mol.<sup>-1</sup> sec.<sup>-1</sup>.

Most of the reactions in the category comprising this section are oxidations. Scheer & Taylor (72) described the oxidation of propane induced by azomethane on activation by light. The induced oxidation takes place as low as 35°C., but the induction factor is small. It increases above unity when the temperature is greater than 200°. The phenomenon of successive cool flames appears in the higher temperature range. Bailey & Norrish (73) made analyses of the products of the cool flame combustion of hexane. Peroxides except perhaps  $H_2O_2$ , do not survive the cool flame. The authors suggest aldehydes, which are present in fair abundance, as the agents activating the blue flame. Harding & Norrish (74) ascribe to the particular aldehyde  $CH_2O$  the role of the agent producing the degenerate branching chain characteristics of the oxidation of  $C_2H_4$  at 400°. The conclusion is supported by the parallel changes in activation energy with temperature observed for the oxidation of  $C_2H_4$  and of  $CH_2O$ . Peroxides are excluded as storers of the chain-branching process, since they do not accumulate sufficiently. A complete mechanism is discussed which incorporates earlier work, and offers:  $H_2CO + O_2 \rightarrow HCOOH + O$ ,  $O + C_2H_4 \rightarrow CH_3 + H + CO$ , as chain-branching steps.

Shtern & Polyak (75) made a thorough investigation of the oxidation of propylene, including a detailed analysis of products, and discussed the mechanism of the reaction. Burgoyne & Kapur (76) analysed products resulting on the oxidation of  $C_2H_4O$  above and below the cool flame region, and developed the rate laws for the consumption of  $C_2H_4O$ : approximately  $\propto (C_2H_4O)\sqrt{(O_2)}$  at 298°, and approximately  $\propto (C_2H_4O)$  at 420°C.

Eastwood & Hinshelwood (77) measured the relative rates of oxidation of a variety of ethers, using the maximum rate of pressure increase as index of the reaction rate. Rates increase in the order: pentane < methyl ether < methyl ethyl and methyl propyl ether < propyl ether < ethyl ether. A survey of the rates of oxidation of aliphatic amines was conducted by Cullis & Isaac (78) also using the maximum rate of pressure increase as reaction index. Some general observations made are that introduction of  $NH_2$  into a hydrocarbon increases the rate, as does increase in chain length and decrease in branching.

As in systems already described, the use of inhibitors is a powerful means of isolating reactions also in oxidation processes. Farmer & McDowell (79) studied the oxidation of aldehydes inhibited by alcohols, and discussed the results with reference to the mechanism following, parts of which were established by earlier work:



Chamberlain & Walsh (80) concluded that the inhibiting effect of lead tetraethyl in the oxidation of di-*iso*-propyl ether is due to the formation of PbO. The formation of a fog of PbO in the reaction was proven, and finely divided oxide, but not all solid lead compounds exert a strong inhibitory effect when added. An important clue to the action of lead tetraethyl is that the effect continues in a vessel once the substance has been added, even after continued evacuation.

The reaction of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  was studied by Robinson & Smith (81). The indications are that the reaction is homogeneous only in part, and that the initial step involves the decomposition of  $\text{N}_2\text{O}$ , rather than attack of  $\text{CH}_4$  by it. Cadle & Schadt (82) found the reaction of  $\text{O}_3$  and olefins to be complex, with ratio of olefin to ozone variable, reaching values of 3 in the case of ethylene. The initial rates, however, were observed to be first order in each reactant, and independent of the surface/volume ratio. An interesting feature of the kinetic results is that the temperature coefficient is close to unity, hence the specific rate has a very low  $A$  factor. As possible explanation of the low  $A$  factor is the spin change which takes place if  $^3\Sigma\text{O}_2$  is liberated in the rate determining step. In a previous such examination (83) of a reaction of  $\text{O}_3$ :



the  $A$  factor was observed to be normal.

*Explosions and flame phenomena.*—Warren (84) has made a definitive study and theoretical analysis of explosion limits in hydrogen and oxygen mixtures, varying the surface, vessel size, composition, and carrying the variation of temperature high enough to include the third explosion limit. Existing equations defining the limits were amended and extended, resulting in the general form:

$$\begin{aligned} [(\text{H}_2) + a(\text{O}_2)] + \frac{b}{(\text{O}_2)[(\text{H}_2) + E(\text{O}_2)]} + \frac{c}{(\text{H}_2)[(\text{H}_2) + F(\text{O}_2)]} \\ = K + l(\text{O}_2)^{1/2} + m(\text{H}_2)[(\text{H}_2) + G(\text{O}_2)]. \end{aligned}$$

The first term provides for the intermediate pressure limit, the next two on the left for the low pressure limit, the last term on the right for the third explosion limit,  $K$  is a constant depending only on temperature, and the term



$I(O_2)^{1/2}$  allows for second-order branching. The new features are the introduction of the third term on the left, which provides for the destruction by diffusion to the walls of the radical attacking  $H_2$ , the factors  $E$  and  $F$  which provide for the differing effect of  $O_2$  and  $H_2$  on the diffusion coefficients of the radicals, and the third explosion limit term adapted from Willbourn & Hinshelwood (85), which arises from radical regeneration (e.g., the inert radical  $HO_2$  being made active by  $HO_2 + H_2 \rightarrow H_2O + HO$ ). In the second paper Warren calculates theoretical values of the various parameters, compares them with experimental values, and discusses the mechanism in terms of specific reactions. The theory of the three explosion limits was also dealt with by Akulov (86).

Egerton & Thabet (87) [see also Powling (88)] described a burner which produces a flat flame uninfluenced by contact with surface and makes possible measurement of flame velocities near the lower limit. The flat flames are stable only over a narrow range of composition and when enriched in  $O_2$  adopt cusped forms. The effect of additives (ethyl nitrate, ethyl alcohol, ethyl ether, and acetaldehyde) on the lower limit, and on burning velocity was studied. Their only effect appears to be as a fuel component. Cellular flames are described and discussed by Manton, von Elbe & Lewis (89).

A point to which Egerton & Thabet referred, and which has been prominent in a number of papers, is the question of whether burning velocities are determined by diffusion of heat or of radicals. Walker & Wright (90) applied the theory based on the thermal mechanism to the data for 36 hydrocarbons, including alkanes, alkenes and alkynes, and found the agreement to be about as good as for the radical diffusion theory. A test of mechanism of the type is not entirely satisfactory, since a parameter in the calculations, the activation energy, is not known for the different hydrocarbons, but a constant value of 40 kcal. was assumed. McDonald (91) pointed out that the radical-diffusion theory would predict the same flame speeds in dry  $CO-O_2$  and dry  $CO$ -air mixtures. For a mixture 80 per cent  $CO$  and 20 per cent air, 27 cm. sec.<sup>-1</sup> was measured, and for 47 per cent  $CO$ , 53 per cent air, 14.9. Other studies favor the radical diffusion theory. Wheatley & Linnett (92) observed the effect on burning velocity in acetylene-oxygen mixtures of including diluent gases, and found the burning velocity to decrease in order: He, A,  $N_2$  and  $CO_2$ . They concluded that the effect of A in comparison to He was greater than could be accounted for on any theory based on heat transfer as the rate controlling step. Since the theory for radical diffusion is only approximate, a conclusive test of this mechanism was not made. The variation observed is sharper than the square root of diffusion coefficient indicated by the theory, and appears to vary as the first power of the diffusion coefficient of hydrogen atoms. Cooley & Anderson (93) also favor propagation by H atoms in hydrogen-bromine mixtures. In introducing their work on hydrogen-bromine mixtures, Cooley, Lasater & Anderson (94) pointed out the suitability of this system for fundamental study, since the chemical mechanisms are well understood. Burning velocities are low, *ca.* 30



cm./sec. (as compared to *ca.* 1000 cm./sec. for  $H_2+O_2$ ). The maximum flame temperature is reached at 48–50 per cent  $Br_2$ , but the maximum burning velocity is at 42–44 per cent  $Br_2$ . Van Tiggelen (95) gives a theoretical discussion of burning velocity as involving thermal initiation of chain branching, and applied the theory to data on  $H_2-O_2-N_2$  mixtures.

Kistiakowsky, Knight & Malin (96) made an interesting application of data on the velocity of detonation waves in mixtures of  $C_2N_2$  and  $O_2$ . The excellent agreement of the data obtained for  $C_2H_2$  and  $O_2$  mixtures (97) as well as  $H_2-O_2$  mixtures (98) with the Chapman-Jouguet equations establishes confidence in the theory as applied to reproducible consistent data of the type obtained also for the  $C_2N_2-O_2$  system. Among the parameters affecting the detonation velocities are the dissociation energies of gases appreciably dissociated under the conditions obtaining in the wave. Of the possible choices for  $D_{N_2}$ ,  $D_{CO}$  and  $D_{CN}$ , agreement was found only using the values 9.76, 11.1 and 7.6 e.v. respectively, with the results not very sensitive to the value of  $D_{CN}$ . Steady detonation waves of the calculated velocity are observed also with mixtures of CO and  $O_2$  (99), containing enough  $H_2$  (>1 per cent). When the amount of the catalyst is reduced, the values of wave velocity fluctuate widely, pulsating waves are observed, the wave front is no longer normal to the tube axis and moves with changing orientation. The transition from the steady to the irreproducible behavior is attributed to the slowness of the chemical changes in the hydrogen-lean mixtures. The authors point out the relation of the phenomena in the unsteady systems to spinning detonations. The subject of spinning detonations received direct attention. Duff & Knight (100) investigated the phenomenon in  $CO-O_2$  mixtures, and Fay (101) published a theory of spinning detonations.

#### REACTIONS IN SOLUTION

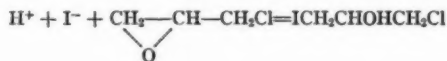
*General aspects.*—Bell & Clunie, using the new method they have developed for measuring rates of rapid reactions (102) studied the rate of hydration of acetaldehyde (103) and made accurate determinations for solutions having large values of the product ( $AcOH$ ) ( $AcO^-$ ). They found no evidence for a term in the rate law containing this product of catalyst concentrations when they subjected the data to an analysis of the type followed by Swain (104). On the basis of their results, Bell & Clunie consider a ternary mechanism unlikely also for the mutarotation of glucose in water, and question the generality of ternary mechanisms. In further work on the subject of concerted displacement reactions, Swain & Brown (105) have found for the mutarotations of  $\alpha$ -D-tetramethyl-glucose (S) in the presence of pyridine (py) and phenol (pl):

$$\text{Rate}/(S) = k_1 + k_2(pl)^2 + k_3(py)(S) + k_4(py)(pl) + k_5(py)(pl)^2.$$

They (106) have also shown that 2-hydroxypyridine is much more efficient than phenol and pyridine used in combination (7,000 times when compared at 0.001 M) in causing the mutarotation of S in benzene. These remarkable

results show as a minimum the benefit of having a polar group besides the catalyst in the activated complex and of having the active groups suitably situated. The question less clearly settled is the role that the third group plays. That an effect besides the presence of the catalyst in the activated complex is important is obvious from the difference in efficiency for a particular catalyst in various media. As a polar medium is progressively diluted by a nonactive solvent terms of progressively lower order in the polar substance can be expected to appear, culminating in a first-order term. Such a series may be involved in the rate law above and is perhaps suggested by the appearance of the fourth-order term. A distinction in thought between Swain's interpretation, and one of the type indicated can be formulated for the reaction in the polar medium. The "solvent" interpretation implies a general orientation of the solvent dipoles about the activated complex; Swain's that a single or perhaps two molecules make specific bonds. In the limit of low polar solvent concentration, the distinction is hazy and can perhaps only be made by comparing the effectiveness of groups of various types in the third order term.

Related to the work discussed, is the question of the distinction between general acid and specific lyonium ion catalyses in media of such low dielectric constant that only associated forms exist, so that the usual kinetic distinction disappears. Roberts, Regan & Allen (107) have discussed the evidence supporting a distinction under these conditions. This includes finding a large decrease in rate on substituting D for H in the acid in a reaction subject to general acid catalysis (solvolysis of diphenyl diazomethane) and a smaller decrease or perhaps increase for one of the other type (solvolysis of ethyl diazoacetate). Additional support for the latter type of mechanism, is the observation that on the ethanolysis of ethyl diazoacetate in  $C_2H_5OD$ , the exchange of the methylene hydrogen is complete. This exchange, showing an equilibrium between acid and substrate involving protons, takes place also in a medium in which the kinetic law becomes (S) (HA). This work makes it appear certain that there is a distinction between two types of acid catalysis which can be demonstrated even when the rate laws are similar. Work by Swain (108) raises serious question of a kinetic distinction between general and specific oxonium ion catalysis even in water. He studied the reaction:



which he chose as a system considered to be a typical one exhibiting specific oxonium catalysis. He observed the rate in 4:1 HOAc/AcO<sup>-</sup> at 4M HOAc to be about twice as great as at the 0.2 M level of HOAc. The hydronium ion path is too small to cause the increase, and Swain concluded by studying the effect of other diluents such as dioxane, that the change in rate is not merely a solvent effect.

Benfey, Hughes & Ingold (109) have now offered a more complete proof

of the peculiar effect of common ion salts on the rate of reactions confirmed by this evidence as of the  $S_N1$  type. In 80 per cent aqueous acetone, 0.1 *M* LiCl retards the solvolysis rate of  $(C_6H_5)_2 HCCl$  by 13 per cent, and 0.1 *M* LiBr increases it 17 per cent; under the same conditions, LiCl increases the rate of solvolysis of  $(C_6H_5)_2 HCBBr$  by 27 per cent but LiBr decreases it 13 per cent. The cross-over of effects makes it unlikely that only general salt influences are involved. The activation energy of reaction of the carbonium ion derived from di-*p*-tolyl methyl chloride with the solvent  $H_2O$  was observed by Hawdon, Hughes & Ingold (110) to be less by 4 kcal. than for the reaction with  $N_3^-$ . Benfey, Hughes & Ingold (111) have found new examples of the anomalous influences of lyate ions on the rates and products of  $S_N1$  solvolyses. Thus, while NaBr and NaI at 0.1 *M* accelerate the solvolysis of  $(C_6H_5)_2 CHCl$  by 20–25 per cent,  $NaOCH_3$  at the same level, if anything, decreases the rate. The lyate ions are also poor competitors against ions such as  $Cl^-$  in reactions with the carbonium ion. Franklin (112) has calculated the heats of activation for some  $S_N1$  reaction paths, among others, the hydrolyses of *t*-butyl chloride and isopropyl chloride. The heats of formation of the ions in the gas phase are available from spectroscopic or mass-spectrometric data, and the heats of solvation were estimated following Latimer, Pitzer & Slansky (113), but making allowance for the shape of the hydrocarbon ions. The activated complex was assumed to have the properties of  $R^+ + X^-$ . The calculations agree with the measured heats of activation within 3 or 4 kcal., and serve to rationalize the participation of  $S_N1$  paths in some but not all solvolyses.

Pearson (114) has presented a review and discussion of heats and entropies of activation of a number of reactions in which ions are formed from neutral molecules in various solvents. He applied Kirkwood's equation for the free energy of a dipole in a dielectric medium to calculate the contribution by interaction with the medium to the free energy of activation of a reaction involving dipoles of typical magnitude, computing also  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  and making comparisons for various media. The calculated quantities follow the trends of those observed for solvents with polar molecules, but the magnitudes of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  calculated are too small for solvents with molecules of low polarity. Pearson suggests that in calculating the entropies, the temperature coefficient of the local, rather than gross dielectric constant be used. In another study dealing with medium effects, Turgeon & LaMer (115) have reinvestigated the kinetics of the reaction of  $OH^-$  with crystal violet in very dilute solution, obtaining accurate data on the variation of rate with ionic strength, solvent composition and temperature. Halberstadt & Prue (116) investigated the kinetic salt effects of tetraalkyl ammonium salts on the hydroxide ion catalysed depolymerization of diacetone alcohol. They were attracted to the problem by the observation that these salts have abnormal activity coefficients, and found the influence on the rate to be abnormal also. Whether added as hydroxides or oxides, the

compounds cause marked accelerations in comparison to KOH and KI, which, in fact, cause slight decreases.

Taft (117) has made a correlation of the rates of hydrolyses of *o*-mono-substituted benzoates, and of aliphatic esters, using the relation  $\log k/k_0 = fA$ .  $f$  is a constant for a reaction series, and  $A$  is a substituent constant. The substituent constant must be assigned separate values to cover the combinations for acid or alkaline catalysed reactions with the substituent in the acyl or alkyl group. As Taft points out, the large number of parameters required makes the correlation much more limited than that achieved by the Hammett relation (118) for a certain field of data, nor does the present correlation include equilibrium data. In another paper, Taft (119) has made a successful application of an idea proposed by Ingold: that the influence of steric factors, but not polar factors, will be the same for the hydrolysis of ester in alkali and in acid, treating a large body of data, and separating polar and steric factors in *ortho* and aliphatic substituents. The equation which erases the steric effect and makes possible the evaluation of the polar factor,  $E_\sigma$ , is:  $\log (k/k_0)_B - \log (k/k_0)_A = E_\sigma(\rho_B - \rho_A)$  where the  $\rho$ 's are reaction constants and B and A represent base and acid. The equation including both the polar factor and the steric factor  $E_s$  is  $\log k/k_0 = E_s + E_\sigma$ , where  $E_s$  is the steric factor. The values of  $E_\sigma$  agree with the qualitative polarity assignments of the English school, and are observed to be parallel for substituents in acyl and alkyl groups. The values of  $E_s$  do not appear to be parallel for changes in the two parts of an ester. The Hammett relation has been applied successfully to published data on the free radical dissociation of tetrazanes by Schwartz & Wilmarth (120). The reaction is much more sensitive to substituent changes than is the decomposition of peroxides. In other work testing the limits of validity of the Hammett relation, substituent effects on substitutions in the ring have been studied. Berliner & Monack (121) obtained data for a nucleophilic displacement of this type, the removal of  $\text{Br}^-$  by piperidine from *para* substituted *o*-nitrobenzenes in piperidine. The reaction rates correlate fairly well with the usual  $\sigma$ -values, but there is considerable scatter, and some reversals of order. The  $\rho$ -value is large, 4.95. A study with a similar goal has been conducted for an electrophilic displacement by Kuivala & Hendrickson (122)



The groups  $\text{OCH}_3$ ,  $\text{CH}_3$ ,  $\text{Cl}$ ,  $\text{Br}$  and  $\text{CO}_2\text{C}_6\text{H}_5$  were used in the *para* and *meta* position and the results display a separate curve for substitution of each position.

The effect of ring size on the rate of substitution in saturated cyclic compounds has been the subject of several investigations. Brown & Borowski (123) studied the rate of solvolysis of 1-chloro-1-methylcycloalkanes, and Fierens & Verschelden (124) the rate of reactions of  $\text{I}^-$  with cycloalkyl bromides. Frequency factors were observed to be fairly constant in each

series, with a maximum variation about 10 fold. The values of  $E$  observed by Brown and Borkowski were: 24.2, 20.8, 24.9, 21.2, 21.1, and 24.2 for  $n=4, 5, 6, 7, 8$ , and 13, and the same trends were recorded by Fieren and Verschelden in the part of the series covered by them. The maximum in rate appears at  $n=8$ , and for large values of  $n$  the rates level off to the values for straight chain compounds. In both papers, the results are discussed fully. Among other factors, Brown and Borkowski discuss the effect of strain on the stability of the reactants, and of the activated complexes of coordination number 3 and 5 for the atom submitting to substitution. Bell & Goldsmith (125) note that 2-carbethoxy cyclohexanone is  $150\times$  less reactive to base catalysis (reaction with  $I_2$ ) than is 2-carbethoxy cyclopentanone.

A point to which repeated reference has been made is the relation which appears to exist in many reaction series between the values of  $E$  and  $A$ . Several striking examples have appeared. In the decarboxylation of substituted picolinic acids in hydroquinone dimethyl ether [Cantwell & Brown (126)] the order of increasing  $E$  (31.1 kcal. to 40.0 kcal.) was also the order of increasing  $A$  ( $\log A$ , 15.63 to 20.66). Even more striking, Szmant *et al.* (127) studying the reaction of diaryl ketone hydrazines in butyl carbitol with the alcoholate ion, found the order of increasing  $\Delta H^\ddagger$  (15.7 to 37.4 kcal.) is with the only one inversion also the order of increasing  $\Delta S^\ddagger$  (-31.0 e.u. to +13.8). For the hydrolysis of ions in the series  $ClC_2H_4RN^+C_2H_4$ , with R isopropyl, ethyl, propyl, methyl, and butyl, Cohen, Van Artsdalen & Harris (128) observed the activation energies to be: 13.4, 17.0, 18.8, 19.8, and 21.4 kcal. and the values of  $-\Delta S^\ddagger$ , 43, 33, 27, 23, and 19 e.u. Another example, involving a fixed reaction, but with the solvent changing is mentioned in the section on complex ions.

A subject which is within the domains of organic, inorganic, and biochemistry is the influence of metal ions on rates of reaction of organic compounds. Their influence in free radical reactions has long been appreciated, but more recent is the appreciation of their effect in substitution processes. During the current year Pedersen (129) published the results of a study of the decarboxylation of oxalacetic acid. He obtained values of the coefficients of each of the terms  $k_0(H_2Ox)$ ,  $k_1(HOx^-)$ ,  $k_2(Ox^{2-})$ ,  $k_3(CuOx)$ . These were (27°, acetate buffer)  $0.34 \times 10^{-4}$ ,  $1.50 \times 10^{-3}$ ,  $4.15 \times 10^{-3}$ ,  $3.5 \text{ min.}^{-1}$  respectively. The comparison of the coefficients  $k_0$  and  $k_3$  shows the strong catalytic effect of Cu(II). The work of Steinberger & Westheimer (130) defines the configuration of the activated complex for processes of this type and provides a dependable basis for discussing the influence of the metal ion. Prue (131) studied the effect of metal ions on the decarboxylation of acetone dicarboxylic acids, the first stage of which is catalysed by metal ions. The extent of complex formation is small and comparisons were possible only at standard concentrations of added metal ion, rather than of the complex. Catalytic activity decreases in order:  $H^+$ ,  $Cu^{++}$ ,  $Ni^{++}$ ,  $Zn^{++}$ ,  $Co^{++}$ ,  $La^{+++}$ ,  $Ph^{++}$ ,  $Mn^{++}$ ,  $Cd^{++}$ ,  $Mg^{++}$ ,  $Co(NH_3)_6^{+++}$ . The affinity of esters of amino acids for metal ions is apparently much greater and the catalysed

rates of hydrolyses with ester at fixed concentration probably represent the specific rates for the complexes. The efficiency in the hydrolysis of glycine ethyl ester decreases in the order:  $\text{Cu}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$  [Kroll (132)] For some acids of this series (e.g., cysteine and histidine) the efficiency of the metal ion may be reduced by complex formation at a point removed from the reaction site. The same relative order can be expected for metal ions acting as acid catalysts in a variety of reactions, since the effect would appear to depend on the ability of the cations to change the electron distribution in the substrate. Furthermore, this order in general is expected to be the same as the order of affinities, since the factor that contributes to association of the metal ion with the substrate in preference to water, is the same as that affecting the electron distributions. Hydrogen ion does not fit in the series, except perhaps when the metal ions may also be limited to a single point of attachment on the substrate.

In a continuation of research on lability of the acid-base systems characteristic of different solvents, Evans, Huston & Norris (133) found the exchange of radiocarbon between acetic acid and sodium plumbic and plumbous acetates to be rapid, rapid also between plumbic acetate and acetic anhydride, but slow between acetic anhydride and acetic acid or acetyl chloride. The results for the solvent pairs shows that dissociation to form ions common to both is slow.

*Mechanism studies with organic compounds.*—Considerable work has been done on configuration changes in reactions which involve carbonium-ion like intermediates. Winstein and co-workers (134) have published in this field work which is impressive in volume and quality (134-143). It will be possible to consider in this review only a small part of the work, arbitrarily selected. One of the conclusions (141) offered is the participation in the solvolysis and racemization reactions of 3-phenyl-2-butyl *p*-toluenesulfonate of an intermediate which is formulated as an ion pair consisting of a carbonium ion and the anion being replaced. This conclusion is based on evidence of the following kind. Racemization of the reactant accompanies solvolysis and the ratio of the rates is independent of the concentration of the *p*-toluenesulfonate ion, showing the phenomena to be intramolecular. Both specific rates are about equally sensitive to changes in the nature of the solvent suggesting the same type of intermediate, or as the simplest interpretation, the same intermediate, with different possibilities for further reaction. The question of the nature of the carbonium ion in the ion pair intermediate, whether cyclic or orthodox, requires evidence beyond the kinetic sort offered. Direct evidence was offered by Roberts *et al.* (144) for the solvolysis 2-butyl *p*-toluenesulfonate. They labelled the 1 position with  $\text{C}^{14}$ , and found only 9 per cent of rearranged product on solvolysis, justifying the

$$\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{CH}_3-\text{CH}-\text{CH}-\text{CH}_3 \end{array}^+$$

conclusion that the cyclic structure  $[\text{CH}_3-\text{CH}-\text{CH}-\text{CH}_3]^+$  is not important for the carbonium ion involved in this change. Stevenson *et al.* (145)

have described interesting observations on the hydrogen exchange and isomerization of hydrocarbons in concentrated sulfuric acid. The results are consistent with a mechanism in which the carbonium ion is generated following the slow oxidation of hydrocarbon, the carbonium ion can remove hydride from another hydrocarbon molecule, forming a new carbonium ion, and the carbonium ion during its life time can undergo isomerizations or exchanges according to well established patterns. Exchanges are observed only with hydrocarbons having tertiary carbons, at least one hydrogen is not exchanged and at least all hydrogens contiguous to the tertiary carbon in the ion are exchanged. Isomerizations observed are understood as migration of alkyl groups along the chain, producing exchange of hydrogens along the walk.

De La Mare & Vernon (146) have been concerned with rearrangements in reactions of the  $S_N2$  type. In the reaction of  $EtO^-$  with 3:3 dichloropropene-1 both simple displacement and displacement with rearrangement ( $S_N2'$ ) occur, the latter reaction yielding *cis* and *trans*-1-chloro-3 ethoxypropene-1. In the corresponding reactions with  $\Phi S^-$  in place of  $EtO^-$ , (147) effects due to further reaction of rearranged product are much reduced. For both  $S_N2$  and  $S_N2'$  the activation energies are 21 kcal. The reaction of  $\Phi S^-$  with  $CCl_3C(CH_3)=CH_2$  (148) was found to be almost entirely by  $S_N2'$ , answering the expectations of the workers, with an activation energy nearly the same as observed in the preceding case.

The new work on elimination reactions has confirmed separate mechanism for *cis* and *trans* elimination. Miller & Noyes (149) compared the rate energetics for elimination from *cis* and *trans*  $C_2H_2Cl_2$ ,  $C_2H_2Br_2$ , and  $C_2H_2I_2$  under the influence of  $CH_3O^-$ . For the *cis* isomers, the activation energy decreases along the series, for the *trans*, it increases. Although in one case elimination from the *trans* isomer has a lower activation energy, in all cases the rate is more rapid for the *cis* form. In this work, as well as that of Cristol and his associates (150), the results are discussed in terms of mechanisms suggested by Cristol: *trans* elimination proceeds by a single step, concerted mechanism, *cis* by the formation of a carbanion intermediate. Cristol and co-workers have reported kinetic data on elimination from compounds of the type  $C_6H_6Cl_6$  (151), from bromo and chloro maleates and fumarates

(152), and from compounds in the series  $(RC_6H_4)_2CH \begin{matrix} Cl \\ C \\ Y \end{matrix} X$  (153) where

X and Y may be hydrogens or halogens. They have determined rate laws, activation energies and studied the effect of varying the solvent. In discussing the data for fumarates and maleates, they propose an explanation based on the higher activation energy for *cis* elimination. The data of Miller and Noyes show such an explanation not to be general. In elimination from 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracenes Cristol & Hause (154) found an example of a system in which *trans* elimination is slower than *cis*.



They attribute this unusual relation to the circumstance that a coplanar arrangement of atoms in the concerted mechanism is not possible in this case. Experiments by Shiner (155) confirm the role assigned to hydrogen in elimination reactions. On substituting D for H in the  $\alpha$ -position of isopropyl bromide, no change in rate of elimination results, but in the  $\beta$ -position there is a 6.7-fold decrease.

Steinmetz & Noyes (156) have studied the catalysis by Br of the change of *cis*-C<sub>2</sub>H<sub>2</sub>Br<sub>2</sub> to the *trans* compound, and the exchange of Br with these compounds. As was observed also for the corresponding iodine system, although the transition states for exchange and isomerization have the same composition, they are distinct. The activation energies for the exchange reactions of *cis* and *trans* are almost equal and are very little greater than  $1/2D_{\text{Br}_2}$ .

An interesting kinetic problem is that of treating data for media such as concentrated sulfuric acid. An example of a successful analysis is that of Brand & Horning (157) for data on the sulfonation of substituted benzenes in fuming sulfuric acid. The active sulfonating agent was assumed to be HSO<sub>3</sub><sup>+</sup>, and the analysis invoked the Hammett acidity function and required data on the pressure of SO<sub>3</sub> above the solutions. Assuming NO<sub>2</sub><sup>+</sup> involved in the equilibrium:  $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 = \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-$  as the nitrating agent, Bonner, Bowyer & Williams (158) were able to account for data on the nitration of  $\Phi\text{NMe}_3^+$  over a 150-fold change in rate produced by changing the solvent from 82 to 89 per cent H<sub>2</sub>SO<sub>4</sub>. The treatment fails to account for the rates near and beyond the maximum rate at 90.4 per cent H<sub>2</sub>SO<sub>4</sub>. In further work on the catalysis of nitration by HNO<sub>2</sub>, choosing conditions to make this path prominent, Blackall, Hughes & Ingold (159) have concluded that N<sub>2</sub>O<sub>4</sub> and NO<sup>+</sup> are the effective agents.

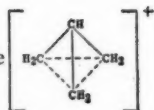
Wibaut & Sixma (160) observed the rates of ozonization of substituted benzenes to decrease in the order  $\Phi\text{C}_2\text{H}_5$ ,  $\Phi\text{CH}_3$ ,  $\Phi\text{H}$ ,  $\Phi\text{F}$ ,  $\Phi\text{Cl}$  and  $\Phi\text{Br}$ . The rates are first order in O<sub>3</sub> and in the acceptor molecule. AlCl<sub>3</sub> increases the rate of reaction in CH<sub>3</sub>NO<sub>2</sub> as solvent. Ozone is presumably an electrophilic agent, and the trend in relative rates is consistent with this view.

Taylor & Feltis (161) obtained precise results on the hydrolytic decomposition of *p*-tolyl diazonium hydrogen sulfate, making use of an apparatus designed to reduce error due to gas supersaturation. Lewis & Hinds (162) claim a second-order displacement reaction for bromide ion on *p*-nitro-diazonium ion, basing their conclusions on kinetic data covering a range in bromide ion concentration from 0 to 6 M, over which the rate increased 80 per cent. Sodium nitrate at 4 M decreases the rate 19 per cent. Zollinger (163) has published a review of data on kinetics of diazo coupling reactions.

Bergstrom & Siegel (164) found the rate of solvolysis of cyclopropyl-methyl benzene sulfonate to be independent of the concentration of NaOH. On this and other evidence they conclude that an S<sub>N</sub>1 mechanism operates,



explaining it on the basis of the stability of an ion of the type

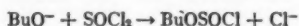
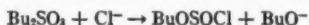


Buess-Thiernagand & Fierens (165) offer as evidence for an  $S_N2$  mechanism in the methanolysis and butanolysis of butyl and methyl esters of propionic and acrylic acid, the observation that the activation energy for the acrylates exceeds that for propionates, suggesting that on a mechanism involving  $RCO^+$  the reverse relation would hold. Berliner & Altschul (166) found good correlation of data on the hydrolysis of substituted aromatic anhydrides in 75 per cent dioxane with Hammett's equation. The substituent effects are consistent with the view that the rate determining step involves a nucleophilic attack by water.

Wyatt & Kornberg (167) have reinvestigated the isomerization of  $NH_4OCN$  in water and have improved on the chemistry of previous work. According to their findings, the amount of carbonate is much greater than admitted in earlier studies. In 0.01  $M$  solution, carbonate amounts to 50 per cent of the urea, but it decreases in importance as the concentration of the  $NH_4OCN$  increases. Allowing for the formation of carbonate calls for a 40 per cent decrease in the accepted value for the specific rate of urea formation.

Morse & Tarbell (168) have compiled and extended data on the kinetics of hydrolysis of thioacetates. In the acid hydrolysis of trityl thiolacetate, scission occurs at the alcohol carbon, but with alkyl and benzyl thiolacetate scission takes place at the acid carbon. For the former process,  $E$  and  $\Delta S^\ddagger$  are  $29.7 \pm 0.6$  kcal. and  $16.2$  e.u., but for the latter,  $16.3 \pm 0.4$ ,  $19.8 \pm$  kcal. and  $-32 \pm$  and  $-21.6 \pm 0.7$ .

Bartlett & Herbrandson (169) reported novel kinetic features for the reaction of thionyl chloride and dibutyl sulfite. The reaction was studied in nitrobenzene at  $25^\circ$ . The rate is very sensitive to chloride, and is first order in the catalyst concentration. The kinetics with respect to reactants are complicated but are consistent with the ionic chain mechanism:



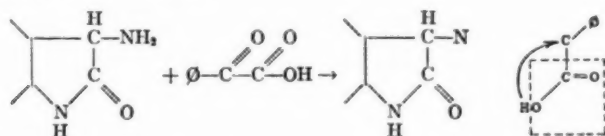
Hydrolyses at acid linkages other than C have received attention. Of the numerous papers in this area containing features of interest only two will be reviewed, even briefly. Baker & Easty (170) studied the hydrolysis of methyl nitrate in aqueous ethyl alcohol, separating simple hydrolysis, elimination to form olefin and formation of aldehyde and nitrate. The alkaline hydrolysis of Me, Et and *i*-propyl nitrates follow second-order laws, but for *t*-butyl nitrate, the rate is independent of  $OH^-$  from 0.09  $M$   $OH^-$  to somewhat acid solution. There is evidence for the incursion of a first-order path for *i*-propyl nitrate in 60 per cent alcohol. Changing to water as solvent

increases the rate for *t*-butyl greatly, slightly for *i*-propyl, and causes a slight decrease for the methyl and ethyl esters. The elimination reaction for ethyl nitrate (27 per cent) and *i*-propyl nitrate (14 per cent) is observed only in alkali. With *t*-butyl nitrate, it is 50 per cent in extent at 60°, and takes place in alkali and neutral solution. The carbonyl elimination runs parallel to that of olefin. Koshland (171) has given a convincing discussion of the mechanism of hydrolysis of acetyl phosphate. The specific rate-pH profile shows catalysis by H<sup>+</sup> and OH<sup>-</sup> at the extremes, and a wide "water" region which exhibits a change in rate concomitant with the change from doubly negative to singly negative ions (latter slower). Since the water region is unusually wide, the author argues that this indicates a change in mechanism for the water reaction, a phenomenon proven for  $\beta$ -butyrolactone and  $\beta$ -propiolactone, which also exhibit this feature. The change in mechanism proven for the latter systems involves the point of attack of the incoming base. Since P—O cleavage occurs in the intermediate pH range, presumably C—O cleavage occurs at the extremes. The hydrolysis is catalysed by Mg<sup>++</sup>, Ca<sup>++</sup>, and pyridine. Since the catalysis by pyridine compared to that of aniline is as expected in view of their relative strengths as bases, Koshland concludes that attack is at the same site, proven to be C for aniline.

Twigg *et al.* (172) have found that the kinetics of the change:  $\text{ClCH}_2\text{CH}_2\text{OH} + \text{OH}^- = \text{C}_2\text{H}_4\text{O} + \text{H}_2\text{O} + \text{Cl}^-$  as well as other properties of the systems show that the equilibrium  $\text{ClC}_2\text{H}_4\text{OH} + \text{OH}^- = \text{ClC}_2\text{H}_4\text{O}^- + \text{H}_2\text{O}$  is established rapidly, and that the equilibrium quotient is 0.37 at 20°. It is interesting that the adjacent chlorine increases the acidity of the alcohol enough to make the ion accessible at reasonable base concentrations.

Glew & Moelwyn-Hughes (173) have made a careful study of the kinetics of hydrolysis of methyl fluoride in neutral and alkaline solution. Specific rates for both the first order and second order processes were determined. While the rate of hydrolysis by either path is slower than that of the other methyl halides, the activation energies are the lowest in the series. The authors present a detailed model for the hydrolysis reaction. Chapman & Levy (174) found the hydrolysis of *t*-butyl and of *t*-amyl fluoride to be catalysed by acid.

Schachat, Becker & McLaren (175) have described an organic decarboxylation catalyst, and have studied the kinetics of the system. The catalyst used was 3-amino-2-naphthoxindole, and the substrate phenyl glyoxylic acid. The mode of action is:



Rearrangement and cleavage as indicated yield CO<sub>2</sub> and a Schiff's base,

from which the reactive intermediate is regenerated by replacing the aldehyde with a substrate molecule. In addition to these changes, there is a gradual consumption of the catalyst by the aldehyde products.

Smith, Schwartz & Wheland (176) have submitted a conclusive proof of an intramolecular mechanism for a benzidine rearrangement. The rearrangement took place in a mixture of 2-methylhydrazobenzene with  $C^{14}$  in the side chain and 2,2-dimethylhydrazobenzene. No radioactivity was found in the product 3,3-dimethylbenzidine.

*Substitution at metal ion centers.*—The number of papers published in this field, though still small, shows the development of interest in an important, but largely neglected field. Until 1945, only twenty or so papers offering quantitative rate data had been published. Since the rates of many of the reactions are conveniently measurable, and since the field offers as attractive features the possibility of varying the nature of the central ion and of studying molecules of various types of geometry, increasing activity is certain to follow growing awareness of the possibilities.

In a general survey of the labilities of complex ions, Taube (177) discussed particularly the influence of electronic structure of the central ion on this property. A good correlation exists, which can be rationalized by considering the relative energies required to form the activated complex from the reactants for different electronic structure types. The common classification of complex ions as "covalent" or "ionic" was criticized, and as a more valid and useful distinction was suggested that involved assigning them to classes termed "inner orbital" and "outer orbital." In the former class,  $d$  orbitals of lower quantum number are hybridized with  $s$  and  $p$  of unit higher quantum number in accommodating the shared electron density; in the latter,  $d$  orbitals if any, are of the same quantum number as the  $s$  and  $p$ . Considering the first class, one or more vacant inner  $d$  orbitals result in a complex ion which is relatively labile, presumably because a stable  $d$  orbital is available in making an activated complex of higher coordination number; if all are occupied, rates of the substitution are much slower. For the "outer orbital" class,  $S_N1$  mechanisms appear reasonable in many cases.

All the kinetic data on substitution reactions on complex ions thus far published deal with systems in which water is a reactant or product as well as solvent. Thus, there is no kinetic basis for distinguishing between  $S_N1$  and  $S_N2$  mechanisms, both of which fit the kinetic laws. Rutenberg & Taube (178) observed that the rate of exchange between  $Co(NH_3)_5H_2O^{+++}$  and water is diminished when reaction to form the sulfato complex takes place simultaneously, and concluded from this that the mechanism is  $S_N1$  at least in part. By arguments based on comparisons of rates of aquation for ions of the type  $Co(A-A)_2Cl_2^+$  (with various chelating groups  $A-A$ ) Pearson, Boston & Basolo (179) concluded that the data favor an  $S_N1$  mechanism. Even if the partial conclusions are accepted for the reactions mentioned the question is open in others, not only for different central ions, but also for  $Co(III)$  when other groups are present.

Plane & Taube (180) studied the kinetics of a simple substitution process, the exchange of  $\text{H}_2\text{O}$  with  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ . The rate is first order in  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ , and in the concentrated salt solutions used, depends on the identity and concentration of the anion. With  $\text{Cl}^-$  present, the rate was shown to be more rapid than replacement of  $\text{H}_2\text{O}$  by  $\text{Cl}^-$ . The activation energy,  $\sim 23$  kcal., is "normal" for  $\text{Cr}(\text{III})$  complex ion reactions, and the  $A$  factor is normal. The exchange is catalysed by  $\text{Cr}^{3+}$ ,  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Ce}(\text{IV})$ . Bjerrum & Poulson (181) have begun important experiments in complex ion kinetics. By working at low temperature ( $-75^\circ$  in  $\text{CH}_3\text{OH}$ ) they have found rates measurable also for the more labile systems. They report the activation energy of  $\text{Fe}^{3+} + \text{CNS}^-$  to be 13 kcal., which may be contrasted with 25 kcal. found for  $\text{Cr}^{3+} + \text{CNS}^-$ . Another way to make rates accessible for central ions ordinarily labile with respect to substitution, is to choose sufficiently complex ligands. Ackerman & Schwarzenbach (182) observed readily measurable rates for the reaction of  $\text{Cu}(\text{II})$  and  $\text{CdY}^-$  to form  $\text{CuY}^-$  and  $\text{Cd}(\text{II})$  ( $\text{Y}^-$  is ethylenediamine tetracetate). Their rate law shows that transfer of  $\text{Y}^-$  to  $\text{Cu}(\text{II})$  can take place by direct attack of  $\text{CdY}^-$  by  $\text{Cu}(\text{II})$ , as well as by preliminary dissociation of  $\text{CdY}^-$ . Acid facilitates both paths. Jones & Long (183) found the exchange between  $\text{Fe}^{2+}$  and  $\text{FeY}^-$  too rapid to measure, but with  $\text{Fe}(\text{III})$  in the corresponding system the rate law was determined. This has the form:  $R = 0.47 (\text{FeY}^-)(\text{H}^+)^3 + 0.015 (\text{FeY}^-)(\text{Fe}^{3+}) + 0.14 (\text{FeY}^-)(\text{FeOH}^{2+})$  mol. $\text{l}^{-1}$  min. $^{-1}$ . As in the work previously cited, there is evidence for exchange by direct reaction of the complex ion and uncomplexed ion. The first term, however, implies a rate determining loss of  $\text{Y}^-$  from the complex, rather than an equilibrium as in the  $\text{CdY}^-$ - $\text{Cu}^{2+}$  case. The rates of aquation and hydrolysis of a number of  $C$  substituted acetatopentamminecobaltic (III) ions were measured by Basolo, Bergmann & Pearson (184) and found to be independent of the size, but dependent on the base strength of the ligand. A tracer result obtained by Hunt, Rutenberg & Taube (185) is of interest in this connection. In the reaction:  $\text{Co}(\text{NH}_3)_5\text{CO}_3^+ + 2\text{H}^+ = \text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+} + \text{CO}_2 + \text{H}_2\text{O}$ , the  $\text{C}-\text{O}$ , not the  $\text{Co}-\text{O}$  bond is severed. Experiments by Atkins & Garner (186) on  $\text{Zn}^{2+}$ - $\text{Sn}(\text{II})$  complex exchanges, by King & Garner (187) on  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ - $\text{Cr}(\text{III})$  complex exchanges, and by West (188) on  $\text{Co}(\text{II})$ - $\text{CO}(\text{II})$  and  $\text{Co}(\text{III})$  complex exchanges have added to qualitative information on the influence of ligand structure and electronic structure on rates.

The new results of Schweitzer & Lee (189) on the racemization of *tris*(2,2-di-pyridyl)  $\text{Ni}(\text{II})$  are consistent with older data and extend the temperature range investigated. They lead to  $1.6 \times 10^{-15} e^{-21,900/RT}$  min. $^{-1}$  as the specific rate-temperature function. Both  $\text{HCl}$  and  $\text{NaOH}$  enhance the rate, producing a limiting *ca.* 2-fold increase in dilute solutions, 0.03*M*. The effects are not understood. For *tris* (1:10-phenanthroline)- $\text{Ni}(\text{II})$ , Davies & Dwyer (190) found the specific rate as  $1.5 \times 10^{15} e^{-24,900/RT}$  min. $^{-1}$ . Slight variations in rate were produced by various salts,  $\text{OH}^-$  producing some acceleration. The configuration of the activated complex, and the role, if any, which the

solvent plays is not known for these changes. Schweitzer and Lee studied mixed solvents, adding acetone, dioxane, methyl alcohol or ethyl alcohol to water, and although changes in rate were produced, no definite conclusions on the role of solvent resulted. Schweitzer & Rose (191) have obtained new data on the racemization of  $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ , confirming a low activation energy ( $\sim 13$  kcal.) and a low  $A$  factor ( $\sim 10^5 \text{ min.}^{-1}$ ) for the reaction. The influence of changes in solvent on this reaction is remarkable. On adding  $\text{CH}_3\text{OH}$ , to water,  $E$  remains about constant,  $A$  decreases slightly. On adding  $\text{C}_2\text{H}_5\text{OH}$ , however, while the specific rate at  $35^\circ$  remains unaltered, at  $25^\circ\text{C.}$ , a marked decrease takes place. The activation energy calculated for 30 per cent  $\text{C}_2\text{H}_5\text{OH}$  is 26 kcal. (compared to 13 in water).

The study by Wilmarth & Baes (192) on the catalysis of the *o-p*  $\text{H}_2$  conversion by paramagnetic ions is mentioned here, since it is an interesting application of such measurements in probing details of geometry of complex ions. A large part of their study was devoted to complex ions of  $\text{Cr}(\text{III})$ , which almost certainly preserve their first coordination sphere intact. Since the magnetic moments are nearly constant in the series, the operative variable would seem to be the closest distance of approach. There is no correlation of the specific rates with this parameter, if the gross sphere composed by the ligands is taken as a measure of size, but the correlation is satisfactory if the detailed structure of the ligands about the coordination center is considered.

*Oxidation-reduction reactions.*—The choice of systems to be discussed in this section is somewhat arbitrary, some of them having been mentioned elsewhere as, for example, the sulfonation or nitration of hydrocarbons. The realization that many displacement reactions as well as addition reactions such as those of halogens to double bonds are, in fact, also oxidation-reduction reactions as ordinarily defined, is sufficient reason to reject as an irresponsible oversimplification the suggestion that all oxidation-reduction reactions involve as steps one-electron changes (or proceed by free-radical mechanisms). The nonradical nature of many reactions in the categories referred to and in related ones, have been proven. The question of whether a one-electron or two-electron change occurs in an oxidation-reduction reaction is an interesting and important one, and one which can be answered by experiment when a reasonable interpretation of the meaning of the terms is made. It may be useful to define the distinction implied by the terms with reference to net change formally represented as:  $\text{A}^{++} + \text{B} = \text{A} + \text{B}^{++}$ , which we take to proceed by an activated complex of composition  $\text{AB}^{++}$ . The distinction is not concerned with the flow of electrons in the activated complex, but with whether evidence can be found for intermediates  $\text{A}^+$  and  $\text{B}^+$  which may be formed on decomposition of the activated complex. If no evidence can be found for such intermediates, based on known behavior for them, the conclusion is drawn that the intermediates are not formed and the mechanism is described as a two-electron change. The converse demonstration is not as often made because net changes usually involve two-electron

changes, and also because chemical methods are usually less sensitive to the corresponding intermediates than they are to free radicals. The high sensitivity of test systems (e.g., vinyl polymerizations) to free radicals frequently tempts authors to an overstatement of conclusions following a positive test. For a satisfactory conclusion, the fraction of the reaction  $A^{++}+B$ , for example, which proceeds to  $A^++B^+$ , must be determined. It is hardly proper to describe the reaction as a free radical process when only 1 per cent, which may be enough to give a positive test for free radicals, follows that course. It must furthermore be shown that the test system S responds by some act following  $A^{++}+B\rightarrow$ , and not by  $A^{++}+B+S\rightarrow$ .

The general classes of two-electron changes suggested in the previous paragraphs will be added to in this by examples drawn from oxidation-reduction in inorganic systems, including some for reagents which have become notorious in choosing free radical paths. Only a few will be mentioned, comprising work in which the question was considered and answered, or from which an inference can be drawn with confidence. The following qualify by proceeding principally as  $2e^-$  changes:  $O_3+Cl^-$  (83),  $S_2O_8^{2-}+I^-$  (193) (the one electron path was much over estimated in the work referred to since an incorrect value for the primary efficiency of dissociation of  $I_2$  by light was used);  $I^-+H_2O_2$ , (193)  $Cl_2+H_2O_2$  (194) [the reaction of  $Cl_2$  and  $H_2O_2$  does not induce the reaction of  $H_2O_2+O_3$ , (195)];  $I_2+S_2O_8^{2-}$ , (196)  $CrO_4^{2-}$  isopropyl alcohol (197). The writer regards the question of the primary products in the reaction of  $Fe^{++}$  and  $H_2O_2$  (198) as still open.

Review articles appearing this year describe reactions of both classes. Edwards (199) has written an attractive analysis of kinetic data of a large number of oxidation-reduction reactions of anionic substances which he has interpreted as displacement reactions involving complex ion intermediates. He has also discussed kinetic data on reactions of hydrogen peroxide (200) with anionic reducing agents, treating them as being of the displacement type, and giving a satisfactory interpretation of the role of acids in the reactions. Uri (201) has published a review of reactions of inorganic free radicals, with emphasis on those derived from oxygen. These also have been discussed in a review by Evans, Hush & Uri (202).

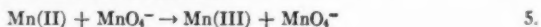
The question of  $1e^-$  versus  $2e^-$  change was referred to in a number of papers presenting new data. Haight & Sager (203) introduced their study of the reduction of  $ClO_4^-$  by  $Sn^{++}$  catalysed by  $Mo(VI)$  by a statement of the question, answered for their system by the conclusion that  $Mo(V)$  is by-passed in the reaction of  $Mo(VI)$  with  $Sn(II)$ . Carter & Davidson (204), on the other hand, proved that  $Br_2$  oxidized  $Fe(II)$ , not to  $Fe(IV)$ , but to  $Fe(III)$  and is reduced to  $Br_2^-$ . The reaction between  $Tl^{+++}$  and  $Fe^{++}$  has been found to be first order in each reactant [Johnson (205); Forchheimer & Epple (206)], and here also the valence change in the rate-determining step is in question. A tentative conclusion that  $Tl(II)$  and  $Fe(III)$  are formed as primary products, is drawn by Forchheimer and Epple from the observation that the reaction of  $Fe^{++}$  with  $O_2$  is induced by  $Tl^{+++}+Fe^{++}$ . Mayo &

Hardy (207) have given an account of work, largely exploratory, defining conditions favoring the free radical versus the polar (2 electron) mechanism for the reaction of  $\text{Br}_2$  with naphthalene.

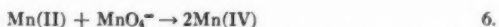
Mechanisms with  $\text{Ti(III)}$  as reducing agent have the simplifying feature that two electron changes are not readily accepted by this agent. Johnson & Winstein (208) observed for the oxidation of  $\text{Ti(III)}$  with sodium anthraquinone  $\beta$ -sulfonate (T) the separate terms in the rate law:  $(\text{Ti(III)}) [k_1(\text{T})^{1/2}(\text{R})^{1/2} + k_2(\text{T})(\text{R}) + k_3(\text{T})^{3/2}(\text{R})^{1/2}]$ . R represents the completely reduced form. The first term corresponds to reaction with semiquinone (S), the second with  $\text{S}_2$  and the third with ST. In a study of catalysis by quinones and phenazines of the reactions of  $\text{Ti}^{+++}$  and  $\text{I}_2$ , Johnson & Winstein (209) found some systems in which the reaction of  $\text{Ti}^{+++}$  and catalyst was rate determining, some for which catalyst and  $\text{I}_3^-$  was rate determining, and also paths first-order in  $\text{Ti(III)}$ ,  $\text{I}_3^-$  and catalyst.

In a continuation of the productive research on chromic acid oxidation mechanisms which Westheimer is sponsoring, Leo & Westheimer (210) have studied the decomposition of di-isopropyl chromate in benzene. In the absence of water, the decomposition is largely oxidative. Pyridine catalyses the reaction by a path first-order in the base and in the ester. Breaking the C—H bond is involved in the rate controlling step and the function assigned to pyridine is to associate with the proton removed. Cohen & Westheimer (211) studied the oxidation of isopropyl alcohol in acetic acid containing 13.5 per cent ester. The kinetic observations are in general similar to those in water. Some features not embraced by this statement are: chloride ion diminishes the rate by forming  $\text{ClCrO}_3^-$ ; the rate of reaction is 250 times as great as it is in water of the same acidity as measured by  $\text{H}_0$  [2,500 as measured by  $(\text{H}^+)$ ].

The reaction of  $\text{MnO}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$  has been studied repeatedly; the number of references in a thorough review of this reaction made by Abel (212) is impressive. A positive conclusion following from new work on the reaction by Malcolm & Noyes (213) is that  $\text{Mn(III)}$  is the only intermediate oxidation state of manganese which accumulates. A more questionable conclusion which the authors draw is that the reaction:



is slow compared to:

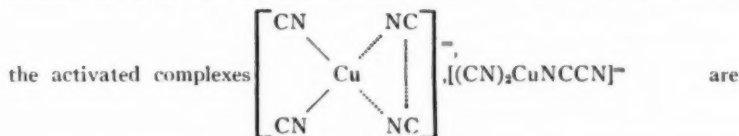


so that the influence of  $\text{C}_2\text{O}_4^{2-}$  as a complexing agent is to alter the rate rather than only the equilibrium involved in reaction 5. Waterbury, Hayes & Martin (214) in a study of the oxidation of  $\text{Mn(II)}$  by  $\text{IO}_4^-$ , arrive at conclusions which differ in part. The system has complex kinetics, evidenced among other things by the autocatalytic behavior (both  $\text{MnO}_4^-$  and  $\text{IO}_3^-$  are involved in reducing the induction period) and by the formation under some conditions of a new species ( $\text{Mn(IV)}-\text{IO}_3^-$  complex) which undergoes further oxidation slowly. The observations are satisfactorily explained if



reactions 5 and:  $2\text{Mn(IV)} = \text{Mn(II)} + \text{Mn(III)}$  are rapidly established equilibria and if reaction 6 and:  $\text{Mn(III)} + 2\text{IO}_4^- \rightarrow \text{MnO}_4^- + 2\text{IO}_3^-$  are rate determining.

In reactions of cationic agents with anionic ones (but not only in these) the formation of complexes in amounts sufficient to affect the kinetics is often a factor. Commenting on a paper by Duke & Courtney (215) on the reaction of  $\text{Cu(II)}$  in  $\text{NH}_3$  aq. with  $\text{CN}^-$ , Connick (216) emphasized the point that although the activated complex may have the same composition as a stable complex, its geometry may be quite different. Thus, in the reaction of  $\text{Cu(II)}$  and  $\text{CN}^-$ , proceeding by the rate law  $k(\text{CuII})(\text{CN}^-)^4$ ,



equally consistent with the kinetics. Complex formation is not necessarily a route to the final products, but may only be a complication.

The use of kinetic data in establishing stoichiometries and stabilities of complexes is well known. An example in the current year is found in the work of Fudge & Sykes (217), and Sykes (218) on the reaction of  $\text{Fe}^{+++}$  and  $\text{I}^-$ . The new work in  $\text{ClO}_4^-$  media confirms the form of the Wagner rate law, and the new evidence of Carter & Davidson (204) makes  $\text{Fe(IV)}$  unlikely in the system, thus establishing the Wagner mechanism. The ions  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  inhibit the reaction and from the observed effects the affinities for  $\text{Fe(III)}$  were estimated. Complex formation may be a factor in the reaction of formic acid and  $\text{Hg(II)}$  studied by Topham & White (219) and may explain the peculiar variation of rate with formic acid concentration which they observed. A complex is certainly formed in the reaction of  $\text{H}_2\text{O}_2$  and  $\text{HNO}_2$ , and its formulation as pernitrous acid is made fairly definite by older work. Halfpenny & Robinson (220) studied the kinetics of the formation of the substance, observing the rate term:  $(\text{H}_2\text{O}_2)(\text{HNO}_2)(\text{H}^+)$  and confirmed the formula  $\text{H}_2\text{O}_2 \cdot \text{HNO}_2 (\equiv \text{HOONO})$  for the complex. The decomposition of the substance initiates polymerization. The conclusion that the mechanism is (largely) a free radical one must, however, be accepted with reserve. Abel (221) discussed the formation of the complex, suggesting a mechanism unnecessarily detailed and complex. The possibility of an intramolecular rearrangement of  $\text{HOONO}$  to  $\text{H}^+ + \text{NO}_2^-$ , in analogy to the mechanism suggested for  $\text{SO}_2$  aq. and  $\text{H}_2\text{O}_2$  (222) seems attractive. The complex  $\text{Se(S}_2\text{O}_3)_2^{2-}$  appears as an intermediate in the reaction of selenious acid and thiosulfate in acid solution [Sorum & Edwards (223)].

Oxidation-reduction reactions have been studied for two systems involving complex ions inert to substitutions:  $\text{Fe(CN)}_6^{3-} + \text{CN}^-$  by Adamson (224) and  $\text{Co(NH}_3)_6^{3+} + \text{Sn(II)}$  in alkali by Pinkerton & Duke (225). In both, the kinetics were complex, the results in the first suggesting the

equilibrium  $\text{Fe}(\text{CN})_6^{-3} + 2\text{CN}^- \rightleftharpoons \text{Fe}(\text{CN})_6^{-4} + \text{CN}_2^-$  preceding the rate controlling step, and in the second, a rate controlling process involving only  $\text{Sn}(\text{II})$ .

The results of Sorum & Edwards (226) on the oxidation of  $\text{S}_2\text{O}_3^{2-}$  by  $\text{S}_2\text{O}_8^{2-}$  confirms the rate law of King and Steinbach. There seems to be no question about the chain character of the reaction, but concern as to whether the chain is intrinsic or carried by adventitious catalysts is not removed by the new work. The limiting rate in the cleanest solutions measured by the present workers is about two times as great as that measured by King and Steinbach. Murib & Ritter (227) have shown the decomposition of nitrosyl disulfonate to follow the kinetics for a chain reaction with degenerate branching. The rate is first order in disulfonate and in hydrogen ion initially, but accelerates rapidly. The autocatalysis is suppressed by sulfamic acid, known to be a good reagent for consuming nitrites.

Of the various paths described for the reaction of  $\text{HOCl}$  with olefinic groups, those second order in  $\text{HOCl}$  are most interesting. The term  $k(\text{HOCl})^2$  has been observed in the allyl alcohol [Israel, Martin & Soper (228)] and crotonic acid reactions [Craw & Israel (229)] but with different coefficients, 8.2 and 4.0 l. mol.<sup>-1</sup> min.<sup>-1</sup> at 25°. Shilov (230) reports for a similar kinetic term in the reaction of allylsulfonate at 0°, 1.6 l. mole<sup>-1</sup> min.<sup>-1</sup>. A puzzling feature of the results obtained by Israel and co-workers is that with ethylcrotonate (231) the term in question is replaced by  $k(\text{HOCl})^2(\text{S})$ , which for the conditions used, conducts less reaction than the term it replaces. Lister (232) reports the term  $k(\text{HClO})^2$  also in the disproportionation of  $\text{HClO}$  in  $\text{ClO}^-$ - $\text{HClO}$  mixtures, with coefficient 1.9 l. mole<sup>-1</sup> min.<sup>-1</sup> at 30°. If all the data reported are accurate, the conclusion must be drawn that the different environments add species to the activated complexes which are not exposed by the kinetic studies.

Schmid & Woppman (233) demonstrated a rate law for the reaction of aniline with nitrous acid which combines the limiting forms observed in earlier work at low acid and at high acid:  $d(\text{RN}_2^+)/dt = k_1(\text{HNO}_2)^2(\text{RNH}_3^+)/k_2(\text{H}^+) + (\text{RNH}_3^+)$ . The rate law follows from a mechanism in which the reaction of  $\text{RNH}_2$  and  $\text{N}_2\text{O}_3$  is rate determining when  $\text{RNH}_2$  is low, but at high  $\text{RNH}_2$ , the formation of  $\text{N}_2\text{O}_3$  controls. Their claim that the same rate law describes the reaction of  $\text{NH}_3$  and aliphatic amines with nitrous acid is not supported by the work of Dusenbury & Powell (234). The latter work has, however, been criticized by Austin *et al.* (235).

Some exchange and tracer results of significance in the mechanisms of oxidation-reduction reactions have been obtained. Jenkins & Yost (236) found the exchange of  $\text{T}^+$  and  $\text{H}_2\text{PO}_2$  to proceed at a rate equal (with allowance for isotope effects) to the rate controlling step in the oxidation of this substance by a variety of agents. The rate controlling step has been considered to be a tautomeric shift of  $\text{H}^+$ . Halperin & Taube (237) made observations using oxygen tracer in the reaction of halogenates with  $\text{SO}_3^{2-}$  which prove direct transfer of oxygen atoms from the oxidizing agent to the reducing

agent. The results support the view that the reduction of  $\text{ClO}_3^-$ , for example, is stepwise, with complete transfer in the stages  $\text{ClO}_3^- \rightarrow \text{ClO}_2^-$ ,  $\text{ClO}_2^- \rightarrow \text{ClO}^-$ , but only partial transfer in the step  $\text{ClO}^- \rightarrow \text{Cl}^-$ . Among the results obtained in studies on other systems (222) is the demonstration that in the reaction:  $\text{HSO}_3^- + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{SO}_4^{2-} + \text{H}^+$  both atoms in the peroxide molecule appear in the product  $\text{SO}_4^{2-}$ . Bothner-By & Friedman (238) obtained evidence suggesting a symmetrical intermediate for the reaction  $\text{NO}_2^- + \text{NH}_2\text{OH}$  in neutral solution, and proving the participation in acid of a path in which the nitrogen remain distinct. Bonner & Bigeleisen (239) proved that the exchange of  $\text{N}_2\text{O}$  with  $\text{H}_2\text{O}$  or  $\text{OH}^-$  is very slow and that  $\text{N}_2\text{O}$  from the decomposition of hyponitrite and of  $\text{NaN}_2\text{O}_3$  suffers no exchange with the solvent. Forchheimer & Taube (240) observed that the oxygen released when ozone decomposes in water under the catalytic influence of  $\text{H}_2\text{O}_2$ , has undergone some exchange with the solvent.

Considerable new work has appeared on reactions commonly represented as involving only electron transfer in the net change, particularly using the isotope tracer technique. Rates have been measured and kinetic analyses made for  $\text{Fe}^{++}\text{-Fe}^{+++}$  [Silverman & Dodson (241)];  $\text{V(III)-V(IV)}$  [Furman & Garner (242)];  $\text{Eu}^{++}\text{-Eu}^{+++}$  [Meier & Garner (243)];  $\text{Co}^{++}\text{-Co}^{+++}$  [Bonner & Hunt (244)];  $\text{Hg}_2^{++}\text{-Hg}^{++}$  [Wolfgang & Dodson (245)]. In all of the studies, influence on the rate by anions was observed. Hornig & Libby (246) studied the catalysis by fluoride of the  $\text{Ce}^{+++}\text{-Ce(IV)}$  exchange. By studying the effect of  $\text{Cr}^{++}$  on the  $\text{Cr}(\text{H}_2\text{O})_6^{+++}\text{-H}_2\text{O}$  exchange, Plane & Taube (180) showed the electron exchange  $\text{Cr}^{++}\text{-Cr}(\text{H}_2\text{O})_6^{+++}$  to proceed at a conveniently slow rate, and to be subject to catalysis by  $\text{Cl}^-$ . Exchanges on the systems  $\text{V(II)-V(III)}$  [King & Garner (247)],  $\text{Mo}(\text{CN})_6^{3-}\text{-Mo}(\text{CN})_6^{4-}$  [Wolfgang (248)], and *tris* (5,6-dimethyl -1,10-phenanthroline) complexes of  $\text{Fe(II)}$  and  $\text{Fe(III)}$  [Eimer & Medalia (249)] were observed to be complete in the time of separation, in most cases using several methods. Past experience suggests caution in drawing any but limited conclusions from results for complete exchange. A recent example is the success of Bonner & Hunt (244) with  $\text{Co}^{++}\text{-Co}^{+++}$  after a history of failure by them as well as others.

Views expressed by some [Dodson (250); Davidson (251)] about the mechanism of these changes favor a chemical interpretation: that electron exchange accompanies atom transfer. This interpretation certainly has a range of validity, as shown by numerous systems in which atom transfers have been demonstrated. Other views, [Libby (20)] which have a solid experimental basis in the occurrence in the gas phase of electron transfer over distances double the viscosity collision diameter, favor a more physical interpretation. The influence of the solvent is included by applying the Franck-Condon Principle to the electron transition. Since both interpretations place requirements on the position and motion of atoms prior to electron transfer, the distinction between the two in principle is not sharp. Useful discussion of the views can only be based on distinctions between specific models for the activated complex. One important distinction is con-

cerned with the distance over which electron exchange is possible in a solvent. It should be pointed out that the rapid exchanges observed (accepting the data at face value) for systems such as  $\text{Mo}(\text{CN})_6^{3-}$ - $\text{Mo}(\text{CN})_6$  do not escape the "chemical" interpretations. The exchanges are not between central ions, but between the molecules as written, and the electron may follow a favorable motion of a positive center such as  $\text{H}^+$  or  $\text{Na}^+$  from one ion to the other. It seems likely, however, that the theory that electron transfer can take place through several layers of solvent will have the greater realm of validity for exchanges between anions. On both views, equivalence of groups in the first co-ordination sphere would appear to be sufficient condition for easy electron transfer between two ions with the same central atoms. To what extent such circumstances are necessary conditions is not clear.

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# CONTACT CATALYSIS AND SURFACE CHEMISTRY<sup>1</sup>

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## INTRODUCTION

The first review in this series by Taylor (1) indicated the main trends of research on contact catalysis and surface chemistry in the years immediately after the second World War and related these trends to the work of the period from 1920 to 1940. The second review by Emmett (2) gave a comprehensive survey of work published during the year 1950 which included the important and stimulating *Discussion of the Faraday Society on Heterogeneous Catalysis* (3). The lapse of two years since the last review makes the problem of selection of material extremely difficult. The principle adopted will be to give a full discussion of some aspects of the subject rather than to attempt to cover the whole field. The first section will be devoted to adsorption with subsections on the thermodynamic aspects, physical adsorption, and chemisorption. The second section on reaction kinetics will deal mainly with catalysis on metallic surfaces and in particular the special topic of exchange reactions because a number of important papers have appeared on this topic.

## ADSORPTION

*Thermodynamic aspects and adsorption isotherms.*—Attention has been directed firstly to the methods of evaluating thermodynamic quantities from experimental data and secondly to devising isotherms having a greater range of validity than the BET isotherm. Hill (4) has given a general review of the theory of physical adsorption in which the different thermodynamic approaches are clearly set out, and the difference between differential and integral entropies and heats of adsorption are clearly explained. Hill favors the evaluation of integral quantities on the grounds that such values may be compared directly with values calculated by the methods of statistical mechanics. An illustration of the methods available to obtain integral heats and entropies of adsorption is given by Hill, Emmett & Joyner (5) who considered the system, nitrogen adsorption on graphon, and they obtained interesting confirmation of the validity of the BET surface area by finding a minimum in the integral entropy at a coverage corresponding closely to the BET value of  $V_m$ . Everett (6, 7, 8) has developed a somewhat different approach favoring the evaluation of the more easily obtainable differential thermodynamic quantities. In the second of the three papers Everett considered two possible reference systems to which real systems might be compared. The first of these reference systems was the ideal localized monolayer which leads to the well-known Langmuir isotherm, and the second the ideal

<sup>1</sup> The survey of the literature pertaining to this review was completed in November, 1952.

nonlocalized monolayer where the adsorbed material is considered as a perfect two-dimensional gas. In the third paper he showed that the localized model is much more satisfactory than the nonlocalized model for real systems. This is not surprising because the former takes into account the important factor that a given area of surface will only adsorb a limited number of particles whereas the latter makes no allowance for this. In applying the localized model Everett divided the differential entropy of adsorption into two parts: a differential configurational entropy which can be easily calculated provided the extent of the surface is known, and an excess entropy of adsorption. He found that the latter was linearly related to the differential heat of adsorption for a wide range of systems, in fact the relationship was very similar to the Barclay-Butler relationship between the heats and entropies of vaporization of liquids. A useful summary of his conclusions and other aspects of the thermodynamics of adsorption is contained in a report of a conference held in July 1950 [Whitton & Young (9)]; one of the difficulties in reaching fundamental conclusions about heat-entropy relationships for adsorption was stressed by Barrer & Kemball, namely that the experimentally accessible range of free energy values is usually very much less than the corresponding changes in heats and entropies. In other words the average experimental technique is not able to cope with systems where the heat of adsorption is large and the entropy small or vice versa, and any conclusion that there is some compensating relationship such as a linear relationship between heats and entropies may be, in part, caused by the limitations of experimental technique. It must also be emphasized that the fact that Everett found the ideal localized monolayer a satisfactory model does not mean that the adsorption is always localized. As he showed in his second paper several of the mobile equations of state that have been suggested from time to time gave a variation in the entropy of adsorption with coverage which was almost identical with the variation in the case of the ideal localized monolayer. The use of his model in cases where the adsorbate enjoys some mobility may lead to some confusion because part of the translational entropy has been separated in the configurational entropy term and part remains in the excess entropy term. According to the model the differential configurational entropy for adsorption at a half-covered surface is zero. Thus the excess entropy will contain a translation term corresponding to the difference between the three-dimensional entropy of the adsorbate and the differential two-dimensional entropy of the adsorbed material on the half-covered surface. Everett's approach, therefore, although simple to apply, does tend to obscure the distinction between mobile and localized adsorption and is not so informative about the freedom of the adsorbed molecules as Hill's approach.

Barrer & Robins (10) have developed a new adsorption isotherm along the lines of the van der Waals equation of state for gases. Their method of obtaining the isotherm allowed for both vertical and horizontal interactions

between the adsorbed particles whereas the BET isotherm takes no account of the latter. The treatment showed that multilayer formation should take place below the critical temperature and that as the relative vapor pressure of the adsorbate is increased the boundary between a densely populated film and a dilute region moves outwards from the surface. Using the van der Waals constants they showed that the calculated isotherms for nitrogen on plane surfaces may be either Type I or II, according to the Brunauer classification, and that a Type III isotherm may also be obtained with water. Agreement was obtained between their calculated isotherms and observed isotherms for these two adsorbates over a wide range of relative pressure.

Halsey (11) has produced a new multilayer adsorption isotherm which takes the following factors into account: (a) the decrease in the London attraction forces as the distance from the surface increases; (b) the fact that an adsorbed molecule may be situated only at integral multiples of the molecular diameter from the surface; (c) the distribution of sites of varying energy on the surface; and (d) the interaction of adsorbed molecules. Despite the complexity of the problem, by the use of various simplifying assumptions his final adsorption isotherm depends on only three arbitrary constants and is therefore not too unwieldy to be of considerable practical importance. He showed that under certain conditions the new isotherms gave surface areas comparable with the BET area, and under other conditions some explanation of the failure of the BET treatment was obtained.

There have been some attempts to rationalize the Hüttig isotherm, i.e., to find a model which leads to this isotherm. The original derivation was criticised by Hill (12) who showed that the derivation was unsound and if carried out rigorously would lead to the BET isotherm. Ferguson & Barrer (13) attempted a statistical derivation, but this also has been criticized by Hill (4). Barrer (14) has suggested that the isotherm may correspond to a model where lateral interactions between the molecules are taken into account and the distribution of molecules in the different layers is determined by the sorption potential due to the adsorbent surface. In other words, vertical interactions are ignored in obtaining the Hüttig isotherm, whereas horizontal interactions of the adsorbed molecules are ignored in the BET theory. Another idea has been put forward by Theimer (15) who suggested that the so-called second layer molecules are really situated on adsorption centers beside the first layer molecules but separated from them by a sufficient distance so that the interaction is negligible. This concept seems somewhat artificial and lends support to the views of Hill (4) that the Hüttig isotherm should be regarded as empirical. Theimer (16) has produced a modified isotherm by assuming that the chemical potential of molecules in higher layers is dependent not only on the relative pressure of the adsorbate but also on some power of relative pressure and has obtained good agreement with experiment.

Honig & Reyerson (17) have evaluated the distribution of adsorption

energy sites on rutile using data for the adsorption of nitrogen, oxygen, and argon and the method of Sips (18). They found that the distribution was dependent on the adsorbate. However the Sips method must be applied with caution because it assumes that the only effect of heterogeneity is a change in the heat of adsorption and that the entropy of adsorption is not influenced by the type of site. Consequently in view of the heat-entropy relationship formed by Everett (8) it is unlikely that the Sips method will give a true picture of the distribution of energy sites on a heterogeneous surface. It is possible that the method may lead to a distribution of free energy sites, and this may explain why Honig & Reyerson found the distribution to be adsorbate-dependent.

*Physical adsorption.*—One of the major contributions in this field is the calorimetric study of argon adsorbed on rutile by Morrison and his colleagues. By studying the heat capacity of the adsorbed argon at low concentrations Morrison, Los & Drain (19) showed that the argon was behaving as a three-dimensional oscillator up to 25°K. indicating that the adsorption was localized at low temperatures. As the transition to the mobile state occurred at higher temperatures, there was a substantial rise in the heat capacity which, at the lowest concentration studied, attained the value of 11 cal./deg.mole. Morrison & Drain (20) reported a similar rise in the heat capacity for higher concentrations of argon corresponding to multilayer adsorption in the temperature range 65–83°K. This rise was attributed to the fusion of the argon. Drain & Morrison (21) have calculated both integral and isosteric (differential) heats of adsorption and also integral and differential entropies of adsorption for this system up to coverages corresponding to 4.6  $V_m$ . It is interesting that they found a minimum in the integral entropy of the adsorbed argon at a coverage corresponding closely to the BET  $V_m$  [cf. Hill, Emmett & Joyner (5)]. The values obtained for the zero point entropies at low coverages were considerably less than the expected values of the configurational entropy corresponding to localized adsorption on a uniform surface, indicating that the surface was heterogeneous. The technique although laborious is certainly powerful and might well be employed with advantage to other systems involving physical adsorption.

A number of papers have been devoted to the question of determination of surface area. Pickering & Eckstrom (22) adsorbed nitrogen, krypton, argon, carbon monoxide, and carbon dioxide on anatase and showed that for some of these adsorbates cross-sectional areas which differed substantially from the values calculated from the liquid density of the adsorbate had to be assumed in order to obtain consistent values for the surface area by the BET method. They also derived values of the constants required to obtain agreement between the Harkins-Jura areas and the BET areas. Aston & Mastrangelo (23) have suggested that the high density corresponding to the BET  $V_m$  for the adsorption of helium on various adsorbents may correspond to the formation of a double layer and not a monolayer. Schreiner



& Kemball (24) used the BET, Hüttig, and Harkins-Jura methods to determine the surface areas of metallic oxides. The first two methods gave consistent results but the last was found to be unsatisfactory. In order to obtain agreement with the BET or Hüttig areas it was necessary to assume that the Harkins-Jura constants depended on the adsorbent as well as the adsorbate. Barrer, Mackenzie & Macleod (25) have compared areas determined by the BET, Hüttig, and a number of modified BET isotherms. They reached the conclusion that the greater the range over which the isotherm fitted the experimental results the greater was the accuracy of the surface area determined by it.

New light has been thrown by Bowden & Throssell (26) on the conditions under which very heavy layers of adsorbed water are formed. They examined the adsorption of water and other vapors on metallic foils. Provided the foil was carefully cleaned the adsorption of water was no greater than of organic vapors, one molecular layer being formed at a relative pressure of about 0.6, and even at 90 per cent saturation the adsorption did not amount to more than two layers. However if the foil was contaminated heavy adsorption was observed, and they suggested that the heavy adsorption observed by earlier workers might be due to the presence of minute amounts of ionic or hygroscopic material on the surface. They checked the conclusions from their adsorption measurements by the technique of determining the thickness of the surface layer by the reflection of polarized light.

Among the papers on the simultaneous adsorption of two substances there is the work of Innes, Olney & Rowley (27) who have obtained isotherms for mixed vapors of benzene and methanol on activated charcoal. This is a continuation of the earlier work of Innes & Rowley (28) with mixed vapors of carbon tetrachloride and methanol on the same adsorbent. Band & Emery (29) have generalized the BET isotherm for the case of two isotopic species and claim that it will be of use in connection with the adsorption of helium isotopes.

Milligan *et al.* (30) have described a new form of adsorption apparatus by which isotherms may be determined on 15 adsorbents simultaneously; silica springs are used to measure the adsorption. Schreiner & Kemball (31) have investigated the adsorption of a number of vapors on cupric oxide and the oxides of nickel, magnesium, and zinc. Many of the systems showed irreversible adsorption, e.g., ethanol and acetone on all four adsorbents, which was attributed to chemisorption. The reversible systems were examined in detail, and there was found a general parallelism between the differential heats and entropies of adsorption in support of the conclusions of Everett (8). An attempt was made to calculate the differential translational entropy of the adsorbate on a simple model, and comparison with the experimental entropies indicated that the majority of the adsorbates were undergoing nonlocalized adsorption on nickel oxide and magnesium oxide. Evidence of chemical interaction with the surface was also found by Hacker-

man & Cook (32) who adsorbed acids, amines, alcohols, and esters on steel powder.

An interesting approach to the general problem of hysteresis has been given by Everett & Whitton (33). They investigate the relationship between hysteresis and super-saturation in terms of a simple mechanical model. They show that hysteresis can be explained on the basis of the existence of a large number of independent domains at least some of which can exist in metastable states. In particular they point out that adsorption hysteresis will follow if there is an assembly of regions on the surface of the adsorbent upon each of which a slightly different equation of state for the adsorbate is operative; a system of this kind would give rise to hysteresis in the condensation and re-evaporation of the vapor.

*Chemisorption.*—One of the topics which is still unresolved is the difference between clean metallic surfaces produced by evaporation or flashing a wire and the bulk metal catalysts. It is now clear that the clean surfaces although capable of adsorbing a considerable fraction of a monolayer of some gases very rapidly do show activated adsorption at higher coverages. Rideal & Trapnell (34) found a slow up-take of oxygen on evaporated tungsten films after a certain amount of instantaneous adsorption. Tompkins (35) has reported similar results for the adsorption of hydrogen on iron films and has suggested that thermodynamic equilibrium is not established below 150°K. because the final stages of the adsorption process are extremely slow at low temperatures. The chemisorption of methane was found by Kemball (36) to require an activation energy of 11 kcal./mole on evaporated nickel films and only took place at a measurable rate at temperatures upwards of 100°C. Schuit & de Boer (37, 38) have studied the effect of oxygen on the rate of adsorption of hydrogen by a nickel-silica catalyst. With increasing amounts of oxygen on the surface the amount of hydrogen rapidly adsorbed decreased, but the total adsorption was hardly influenced. They suggest the activated adsorption of hydrogen on bulk metal catalysts is associated with contamination on the surface with something such as oxygen. This may well be the reason why bulk catalysts show activated adsorption at lower surface coverages than the evaporated metal surfaces, but in view of the evidence quoted above contamination is not the sole cause of activated adsorption.

The difficulty of preparing clean surfaces of iron has been stressed by Eggleton & Tompkins (39). They measured the accommodation coefficient of neon on iron wires treated in various ways. Their work stresses the usefulness of accommodation coefficient measurements in establishing whether a surface is clean, and they suggest that information about the nature as well as the existence of a chemisorbed gas may be determined by the size of the increase in the accommodation coefficient. They list the values of the coefficient for helium and neon on clean surfaces of platinum, nickel, tungsten, and iron, the values lying between 0.056 and 0.072. Reduction in hydrogen

followed by flashing at 1200°C. was not found to be effective in cleaning the iron wire. Bombardment by neon gave a clean surface only when preceded by bombardment with nitrogen ions. It was suggested that the formation of a nitride layer below the surface prevented the outward diffusion of oxygen from the body of the iron to the surface. The implication that oxide contamination is present on many so-called reduced catalysts has been emphasized by Tompkins (35).

The problem of the rate of chemisorption has been considered by Taylor & Thon (40). They showed that for a great many systems the rate of adsorption can be fitted to the Elovich equation

$$\frac{dq}{dt} = ae^{-\alpha q}$$

where  $q$  represents the amount adsorbed at time  $t$ , and  $a$  and  $\alpha$  are constants. They gave a novel interpretation of this fact. They suggested that the initial action of the gas was the production of a number of sites on the surface capable of adsorbing the gas. During the course of the slow adsorption the sites disappear according to a bimolecular law. Their explanation leads to the correct mathematical form for the Elovich equation to be obeyed, but it is not the only model which would lead to the same equation. The weakness of their theory is that it ignores any change in the energy of activation for adsorption as the surface is covered, i.e., the fact that on a given site the adsorption is more difficult when the coverage is great or alternatively that a more highly activated site is required for adsorption in the latter stages. The grounds for believing that the activation energy for adsorption depends on coverage are good. Not only the experimental work quoted above but also the theoretical considerations put forward by Halsey (41) support the concept. Thus, although the widespread applicability of the Elovich equation is established, not only for bulk adsorbents but also for evaporated metallic films [Tompkins (35)], the interpretation is still open to doubt. However it should be noted that any theory involving increase of activation energy with coverage would lead to a similar type of equation.

The question of the why heats of chemisorption fall as the coverage of the surface is increased is still being given active consideration. Although the major factor in many systems particularly those involving bulk adsorbents may be intrinsic heterogeneity of the surface, the role of induced heterogeneity, i.e., alteration of the bonding power of neighboring sites by the presence of some chemisorbed material, must not be neglected. Boudart (42) has attempted to explain the fall in heat of adsorption by considering the magnitude of the dipoles associated with the chemisorbed layer which in turn are related to the surface potential associated with the layer. However, as with many problems concerned with dipole moments, a knowledge of the dipole moment alone is not sufficient, and very different results are obtained if the dipole is considered as unit charge at the appropriate separa-

tion or a fractional charge at a proportionally greater separation. This factor is neglected by Boudart, and his conclusions are open to objection. If the dipole moment is made up of unit charges the work done in introducing a further charge when the surface potential is  $\Delta\phi$ , will be equal to that potential. This would mean a decrease in the differential heat of adsorption of  $\Delta\phi$  ev and a fall in the integral heat of adsorption of  $0.5 \Delta\phi$  ev. The value for the integral heat of adsorption is in keeping with the expression for the energy of a parallel plate condenser, i.e.,  $\frac{1}{2}QV$ ,  $Q$  being the charge on the condenser and  $V$  the potential. In other words, the total integral heat for the formation of an adsorbed layer differs from the ideal value corresponding to constant heat of adsorption by the energy of the charged condenser which is formed at the surface. On the other hand if the addition of each chemisorbed particle only introduces a fraction of an electronic charge the changes in the differential and integral heat are reduced proportionally. Boudart's equation will only apply if each chemisorbed atom corresponds to the formation of a dipole moment consisting of one-half of an electronic charge at the appropriate separation to give rise to the observed surface potential. This restricts the validity of his conclusions that this induction effect is sufficient to account for the decrease observed in the heat of adsorption with coverage.

One or two other papers dealing with the measurement of surface potential and work function may be mentioned. Mignolet (43) has reported measurements of the surface potential changes when hydrogen is adsorbed on tungsten and chromium. He concludes that there is a substantial reduction in the dipole moments at high coverages and suggests that the fall of the heat of adsorption may be due to a shift of the hydrogen atoms from their position of maximum stability. Bourion (44) has reviewed the different methods available for the measurement of contact potentials. Mitchell & Mitchell (45) have reported new values for the work functions of copper, silver, and aluminium. They used the retarding potential method and measured the contact potential between clean surfaces of these metals and tungsten. An important development in the technique of using the vibrating plate method has been described by Anderson & Alexander (46). One of the difficulties of this method has been the problem of dealing with moving parts in a vacuum system without either impairing the vacuum or causing spurious electrical effects. They have shown that adequate sensitivity can be obtained if the vibrating condenser external to the vacuum system is coupled either in series or parallel with the metals in the vacuum system between which it is desired to measure the contact potential.

An interesting method of detecting the chemisorption of long-chain compounds on metallic foils has been reported by Bowden & Moore (47). An irradiated metal foil is immersed in a benzene solution of the long-chain compound and then treated for a substantial period with dry benzene in a Soxhlet. If the adsorbate is chemically bound to the foil the benzene solution becomes radioactive because of the removal of the radioactive metal linked to the adsorbate.

Zabor & Emmett (48) have followed the adsorption of *n*-butane, *n*-heptane, and *n*-octane on a Houdry S-46 cracking catalyst from room temperature up to the temperature at which decomposition occurred. The adsorption was found to be physical up to 150°C., and even at the temperature at which cracking was beginning to take place the amount adsorbed was very little. They suggest that if the carbonium ion mechanism is to explain catalytic cracking the slow step must be the formation of the ion and that the life-time of the ions must be small. The work raises the whole question of the extent to which it is possible to correlate studies of chemisorption with catalytic activity which has been mentioned by many authors [cf. Tompkins (35); Boudart (42)]. The main point is that for chemisorption the whole surface is under consideration whereas catalytic reaction may be taking place on only part of the surface particularly if the surface is known to be heterogeneous. Even on a homogeneous surface the catalytic activity may be due to the presence of small quantities of short-lived intermediates the existence of which would not be detectable in chemisorption studies.

#### CATALYTIC REACTIONS

A great many papers have been devoted to the study of exchange reactions in the last year or two. A number of different methods have been used to follow these reactions, but it is noticeable that the use of the mass spectrometer as a tool for catalytic research is throwing new light on many problems. The great advantage of the technique is that information is obtained about the amounts of each isotopic species formed, and this can be of considerable importance in elucidating the mechanism of the reaction. Emmett (2) has stressed the importance of studies of reaction kinetics but in some cases the analysis of the products, particularly the initial products, of an exchange reaction can give an even clearer picture of the types of mechanism involved in exchange reactions. Information is also obtained about the nature and reactivity of the radicals formed on surfaces which will have a bearing on many other types of catalytic reactions.

*Exchange between ammonia and deuterium.*—This reaction has been investigated in a number of ways. Weber & Laidler (49, 50) followed the disappearance of  $\text{NH}_3$  by a microwave method on a singly-promoted iron catalyst (#631) and found that the rate of reaction was given by

$$v = k p_{\text{NH}_3} p_{\text{D}}^{1/2} (1 + a p_{\text{NH}_3})^{-2}$$

and that the energy of activation was about 13 kcal./mole. Singleton, Roberts & Winter (51) used the technique, originally employed by Farkas (52) for studying this exchange, of following the change of thermal conductivity as the deuterium becomes diluted by hydrogen. They used sintered films of tungsten, nickel, and iron and found energies of activation of approximately 16, 15, and 20 kcal./mole respectively. Their kinetics differed from the results of Weber & Laidler, the rate of reaction being proportional

to the pressure of deuterium, more or less independent of the pressure of ammonia on tungsten and nickel and showing some decrease with increasing ammonia pressure on iron. However the temperature at which Singleton *et al.* carried out their experiments was considerably higher than the range used by Weber & Laidler which may explain the difference between their results. By using a mass spectrometer Kemball (53, 54) was able to follow the concentration of each deuterio-ammonia throughout the course of the reaction on a number of evaporated metal catalysts. In all cases the initial product was  $\text{NH}_2\text{D}$  and the remaining deuterio-ammonias were formed by successive reaction, one hydrogen atom being replaced at a time. The relative concentrations of each product throughout the course of the reaction corresponded closely to the values calculated from differential equations derived on the following assumptions: (a) one hydrogen or deuterium reaction is replaced at a time; (b) the chance of obtaining a deuterium atom is dependent on the fraction of deuterium in the "hydrogen"; and (c) all four ammonias react at equal rates. This limited the possible mechanisms to three types (i) a dissociation mechanism involving adsorbed  $\text{NH}_2$  radicals; (ii) an associative mechanism involving adsorbed  $\text{NH}_4^+$  ions, or (iii) a direct exchange between an ammonia molecule and one adsorbed deuterium atom. Weber & Laidler (50) claimed that the presence of the square term in the denominator of their rate expression indicated that a Langmuir mechanism, involving reaction between adsorbed species of both gases, was operative. Laidler (55) has suggested that the presence of such a square term in the denominator of the kinetic expression of any catalytic reaction is evidence for a Langmuir mechanism and evidence against an Eley-Rideal mechanism involving one chemisorbed species and one gaseous molecule. However Kemball (54) has pointed out that the Eley-Rideal type of mechanism may still be operative provided two sites are required on the surface and that such kinetics would only exclude an Eley-Rideal mechanism involving one site on the surface. He also showed that there are seven possible combinations of the types of reaction (i) (ii) and (iii) outlined above which would give rise to the kinetics observed by Weber & Laidler for the ammonia-deuterium exchange. Kemball found energies of activation ranging from 5 kcal./mole for platinum to 14 kcal./mole for silver and that there was an inverse correlation between the activation energy and the work function of the metal. This gave some support to the suggestion that the exchange might involve ammonium ions, the formation of which would be easier on a metal with a higher work function. This suggestion must be regarded with caution until more information is available about the work functions of the metal in the presence of the gases because the correlation between energies of activation and the work functions of the clean metals may be spurious. The frequency factors were almost identical on all the metals except tungsten, and the variation in catalytic activity was attributable almost entirely to the differing energies of activation. This is the reverse of the situation for the catalytic hydro-

genation of ethylene on metal films where the activation energy was constant and the frequency factor varied [Beeck (56)]. A comparison between the results of Singleton *et al.* and Kemball shows that sintered films differ from unsintered films not only in surface area but also in catalytic activity.

*Exchange between hydrogen and deuterium and the ortho-para hydrogen conversion.*—The question whether these reactions take place by a Langmuir or an Eley-Rideal mechanism is still unsettled, although further support for the latter mechanism has been produced. Halsey (41) has carried out calculations using the experimental data available for tungsten surfaces and has concluded that the exchange takes place between a chemisorbed hydrogen atom and molecular hydrogen adsorbed on van der Waals sites of varying energy. A valuable point in his paper, which has been stressed above, is his evidence that there will be an activation energy for adsorption at high coverages and that the whole of the observed activation energy cannot be attributed to variation in the heat of adsorption [cf. Trapnell (57)]. Couper & Eley (58) have criticized the calculations made by Trapnell (57) using the Peierls equation and have shown that if the equation is applied in a consistent manner the calculated rates for the Langmuir mechanism are too slow to account for the observed rates of reaction by a factor of  $10^6$ . However the possibility that the Peierls equation is not applicable to this system must not be neglected in which case it may still be possible to account for the observed rate of reaction by the dissociative or Langmuir mechanism; Couper & Eley suggest that this type of mechanism may be of importance at higher temperatures. Couper & Eley (59) have also shown that with different tungsten wires there were variations in both the frequency factor and the energy of activation. They found that there was a linear relationship between the logarithm of the frequency factor and the energy of activation. Poisoning of the surface by carbon monoxide and other gases also gave rise to variation in both these quantities in a similar manner but the slope of the line was different. There are a number of other examples of a linear relationship between the logarithm of the frequency factor and the energy of activation in catalytic reactions, and Kemball (60) has suggested that this behavior may be due to a linear relationship between the entropy and the heat of adsorption of an inhibiting gas along the lines suggested by Everett (8) for physical adsorption. The presence of an inhibiting gas has two effects: the first is well-known and is the increase of the apparent energy of activation to an extent depending on the heat of adsorption, and the second is an increase in the frequency factor to an extent depending on the entropy of desorption of the inhibiting gas. It is quite simple to show that if there is a linear relationship between the heats and entropies of adsorption of a series of inhibiting gases on the same catalyst there will also be a linear relationship between the logarithm of the frequency factors and the energies of activation of a catalytic reaction inhibited by the gases. Similar considerations will apply for the same inhibiting gas on a series of



catalysts. This effect is not confined simply to those systems where a poisoning gas is added but will apply equally to any catalytic reaction where one or more of the reaction gases is moderately strongly adsorbed because the reacting gas is self-inhibiting under such conditions. Couper & Eley (59) tentatively suggested that their observations might be caused by resonance interaction between the sites on the surface, but part of the cause may be a result of the fact that the hydrogen is acting as a self-inhibitor and that the considerations outlined above are applying.

Kummer & Emmett (61) have used the hydrogen-deuterium exchange and the *ortho-para* hydrogen conversion to examine the nature of the adsorption of hydrogen on iron synthetic ammonia catalysts. The conversion occurred rapidly at  $-195^{\circ}\text{C}$ . on a doubly-promoted catalyst, but the exchange reaction was extremely slow at this temperature. It was concluded that there was very little reversible chemisorption of hydrogen at this temperature, and the activity for the *ortho-para* conversion was attributed to the influence of the magnetic field on physically adsorbed hydrogen. It was found that pretreatment of the catalyst with hydrogen at  $100^{\circ}\text{C}$ . reduced the activity for the conversion substantially. On the other hand a singly-promoted catalyst showed much greater activity for the exchange reaction at  $-195^{\circ}\text{C}$ ., and the conversion was not poisoned by hydrogen adsorbed at  $100^{\circ}\text{C}$ . Kummer & Emmett were able to show that neither hydrogen adsorbed at  $-100^{\circ}\text{C}$ . (Type A) nor at about  $100^{\circ}\text{C}$ . (Type B) could be exchanged with deuterium at  $-195^{\circ}\text{C}$ ., and they suggest that a third type of chemisorption of hydrogen must be taking place on singly-promoted catalysts in order to account for the observed exchange reaction at low temperatures.

*Exchange between methane and deuterium.*—Kemball (36) has shown that there are two mechanisms for this exchange on evaporated nickel catalysts. The first had an energy of activation of 24 kcal./mole, involved the formation of adsorbed methyl radical, and produced  $\text{CH}_3\text{D}$ . The second mechanism had a higher energy of activation, involved the formation of adsorbed methylene radicals, and gave mainly  $\text{CD}_4$ , some  $\text{CHD}_3$ , and a little  $\text{CH}_2\text{D}_2$ . The relative amounts of the three heavier compounds and the variation of the relative amounts with the pressure of the gases were consistent with the hypothesis that any methane molecule undergoing the second type of reaction was leaving the surface with a random collection of hydrogen and deuterium atoms. Consequently it was suggested that adsorbed methylene radicals were able to undergo rapid exchange by further dissociation. The stability of adsorbed methyl radicals compared with the reactivity of adsorbed methylene radicals is not unexpected. The methyl radical will be attached to the surface by a single covalent bond and will therefore be fairly stable, but whether the methylene is doubly-bonded to one site on the surface or singly-bonded to two it is likely to be more difficult to form, but once formed more reactive, as indeed was found. Evidence of two mecha-

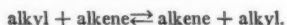
nisms has also been obtained on a cobalt-thoria Fischer-Tropsch catalyst by Thompson, Turkevich & Irsa (62) because the initial products were mainly  $\text{CD}_4$  and  $\text{CH}_3\text{D}$ . Kemball (60) has also used evaporated films of tungsten, palladium, rhodium, and platinum finding in each case that both mechanisms were operative although the relative importance of the mechanisms varied considerably. The energies of activation on tungsten were much lower than on the other metals, and this was attributed to a low energy of activation for the adsorption of methane on tungsten [cf. Kemball (36)].

*Exchange of other saturated hydrocarbons and deuterium.*—The paper by Thompson, Turkevich & Irsa (62) contains an account of some experiments with ethane, propane, butane, and isobutane on the same cobalt-thoria catalyst at  $183^\circ\text{C}$ . The main products with ethane were  $\text{C}_2\text{H}_4\text{D}_2$  and  $\text{C}_2\text{D}_6$  and with the other three hydrocarbons the initial product was chiefly the completely deuterated compound although considerable amounts of the compounds containing one hydrogen atom were also formed because of the dilution of the deuterium by hydrogen. A considerable amount of further experimental work will be necessary before the mechanism of these exchanges is fully understood. In contrast Kander & Taylor (63) have reported that the initial products contain only a few deuterium atoms when propane was allowed to exchange with deuterium on platinized platinum at  $20$ – $40^\circ\text{C}$ . The mass spectra of their products suggested that the secondary hydrogen was more easily exchanged than a primary hydrogen. All the heavier propanes appeared in the later stages of the reaction.

*Exchange of acetylene and methyl-acetylene with dideutero-acetylene.*—Bond, Sheridan & Whiffen (64) followed the production of  $\text{C}_2\text{HD}$  from  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{D}_2$  on nickel catalysts at  $40$ – $100^\circ\text{C}$ . using infrared spectroscopy to analyze for each compound. They found that an energy of activation of  $10.7$  kcal./mole was required and that the rate of reaction was dependent on the  $0.65$  power of the total pressure. They concluded that a dissociative mechanism was unlikely because acetylene inhibits the *ortho-para* hydrogen even more strongly than ethylene suggesting that surface concentration of hydrogen atoms must be small. Furthermore, there was no evidence of loss of activity of the catalyst through polymerization of the acetylene which would have been likely if dissociative adsorption were occurring. It was suggested that exchange was taking place directly between a physically adsorbed molecule and a chemisorbed molecule and that the dipole moment of the carbon-hydrogen linkage in acetylene was an important factor. The reaction between methyl-acetylene and dideutero-acetylene took place under similar conditions, but only the lone hydrogen of methyl-acetylene was exchangeable. No exchange was observed between allene or ethylene and dideutero-acetylene under conditions which gave rapid exchange between the acetylenes.

*Reactions between olefines and deuterium.*—With olefines and deuterium the situation is complicated because exchange may occur simultaneously

with addition. Wagner *et al.* (65, 66) have reported some interesting results with *cis*-2-butene and deuterium on a nickel catalyst at  $-78^{\circ}\text{C}$ . Although no deuterio-olefines were formed and no hydrogen was returned to the gas phase, several deuterio-butan-2-ols were produced. The distribution of the butan-2-ols indicated that some 8 per cent of the olefine was converted directly to  $\text{C}_4\text{H}_8\text{D}_2$  and the remaining 92 per cent of the olefines was deuterated to give a mixture of deuterio-butan-2-ols corresponding to a random distribution of hydrogen and deuterium atoms but with the chance of having a hydrogen four times as great as the chance of having a deuterium, i.e., a mean composition also corresponding to  $\text{C}_4\text{H}_8\text{D}_2$ . They concluded that an important mechanism for alkane formation was the transfer of hydrogen between two chemisorbed alkyl radicals and that hydrogen redistribution could also take place without the intervention of adsorbed hydrogen, i.e., by reactions such as



Markham, Wall & Laidler (67) have formulated a general mechanism for the exchange and hydrogenation of olefines including the types of reaction postulated by Wagner *et al.* (65, 66). They suggest that the kinetics of hydrogenation and exchange should not be identical which is contrary to the observations of Twigg & Rideal (68) on the ethylene-deuterium system. Emmett (2) has already commented on the interesting fact reported by Turkevich *et al.* (69) that the ethylene initially formed from  $\text{C}_2\text{H}_4$  and  $\text{D}_2$  is mainly  $\text{C}_2\text{H}_6$ . A later paper of Turkevich *et al.* (70) does not add greatly to their former paper, and it is unfortunate that the authors still continue to "withhold the mechanism."

Taylor & Dibeler (71) have reported on a number of reactions of 1-butene, *cis*-2-butene and *trans*-2-butene using a nickel wire as catalyst. They investigated hydrogenation, exchange, double-bond shift, and *cis-trans* isomerization. The first three reactions all gave identical kinetics which varied however with the ratio of the pressure of the gases. With approximately equal pressures of hydrogen or deuterium not exceeding 100 mm. the rate was dependent on the square root of both the hydrogen and the butene pressure, but with a large excess of hydrogen, the rate was independent of the hydrogen pressure and directly dependent on the butene pressure. The reactions were inhibited with a large excess of butene. The rate of double-bond shift was faster by a factor of three to five when hydrogen was used than when deuterium was used but no effect of this kind was observed with *cis-trans* isomerization. Their paper also contains some tentative formulation of possible mechanisms to account for the numerous observations that they report.

*Exchange of acetic acid with deuterium.*—Line, Wyatt & Smith (72) have followed the exchange between liquid acetic acid and solutions of acetic

acid in heptane and deuterium using platinum oxide as a catalyst. They found that an energy of activation of 13.6 kcal./mole was required and that the rate of reaction was independent of the concentration of the acid but directly proportional to the pressure of deuterium. The exchange was inhibited by nitrobenzene which was reduced to aniline. It was suggested that the latter reaction was better explained by an Eley-Rideal than by a Langmuir mechanism.

*Hydrogenation of acetylene.*—Sheridan & Reid (73) have followed the hydrogenation of acetylene on rhodium and iridium catalysts. The paper is the sixth in a series of studies of this reaction on metal catalysts and contains a brief summary of the whole series [Sheridan (74 to 78)]. In addition to the formation of ethylene and ethane by direct hydrogenation a certain amount of hydro-polymerization was generally observed. The extent to which hydro-polymerisation occurred varied with the nature of the catalyst but was greater at higher temperature as the energy of activation was slightly larger than the energy of activation for direct hydrogenation. The kinetics of both types of reactions were approximately the same, the rate being proportional to the hydrogen pressure but independent of the acetylene pressure. On a weight basis the order of activity of the different metals was  $\text{Pd} > \text{Pt} > \text{Ni} \approx \text{Rh} > \text{Fe} \approx \text{Cu} \approx \text{Co} > \text{Os} > \text{Ru}$ , the group from iron to cobalt being but weakly active and osmium and ruthenium almost inactive. In contrast to the work of Beeck (56) on the hydrogenation of ethylene there was no direct correlation between the activity of a metal and the percentage of *d*-character in the metallic bonding estimated by the method of Pauling (79). However the basis of comparison was not the activity for the same surface area of catalyst which Beeck used but the less satisfactory criterion of activity for the same weight of catalyst. Sheridan & Reid suggest that it would be interesting to examine the hydrogenation of ethylene on iridium which has a large percentage of *d*-character and yet is a poor catalyst for the hydrogenation of acetylene.

*Hydrogenation of methyl-acetylene.*—Bond & Sheridan (80) have studied the hydrogenation and the hydro-polymerization of methyl-acetylene on nickel, palladium, and platinum. The results were similar to those for acetylene on these catalysts, but the amount of hydro-polymerization was substantially reduced by the presence of the methyl group.

*Hydrogenation of allene.*—The principal reaction was simple hydrogenation on the same catalysts as were used for hydrogenating methyl-acetylene. Bond & Sheridan (81) showed that allene was more strongly adsorbed than propylene because the completion of the hydrogenation to propane did not take place until almost all the allene was used up. Some further information about the competition for the surface by the various unsaturated compounds is given by the same authors (82). By studying the hydrogenation of mixtures they showed that the adsorptions of acetylene, methyl-acetylene, and allene

were of comparable strength, but the adsorption of both propylene and ethylene was weaker. They concluded that their findings were in accord with the concept of adsorption by two-point contact.

*Hydrogenation of cyclopropane.*—In this case Bond & Sheridan (83) found no polymerization but only direct hydrogenation to propane on nickel, platinum, and palladium catalysts. An interesting feature was the difference between the kinetics of this reaction and the others mentioned above. The hydrocarbon was apparently more weakly adsorbed than the hydrogen because the orders of reaction were first and zero with respect to the hydrocarbon and the hydrogen.

#### MISCELLANEOUS

The discussion of reaction kinetics and mechanisms in the last section has been mainly concerned with catalysis on metal surfaces and with attempts to study isolated reactions. Space does not permit a detailed discussion of the work on oxide catalysts and other semi-conducting materials, but a review on these by Roberts & Anderson (84) has appeared recently.

A series of papers by Browning & Emmett (85, 86, 87) giving equilibrium measurements for the system carbon-methane-hydrogen and also methane-hydrogen-metal-metallic carbide for nickel, cobalt, and molybdenum are of interest in connection with the role of carbides in the Fischer-Tropsch synthesis. However, as the authors point out, the surface carbide would probably be more important than the bulk carbide, and little is known yet about the thermodynamic relations for surface carbides.

Many of the papers presented at a conference on "Processes on Crystal Surfaces" held in Germany early in 1952 are of interest in connection with adsorption and catalysis, and they have since appeared in print (88). In particular Schäfer (89) showed that there was a good correlation between the accommodation coefficient of ethane on alloys of platinum and copper and the catalytic activity for the decomposition of ethane into ethylene and hydrogen at high temperatures. He was able to split up the total accommodation coefficient into parts corresponding to different vibrational degrees of freedom of the molecule and found that the catalytic activity of the alloys was greatest when there was the greatest probability for the transfer of energy from the surface to those particular vibrational degrees of freedom of the ethane which would be expected to lead to decomposition into ethylene and hydrogen.

Mention should also be made of a number of general articles which have appeared in the last year. Pichler (90) has given an account of the development of the Fischer-Tropsch synthesis in the last twenty-five years, and Hansford (91) has reviewed the subject of catalytic cracking. Part of the article by Bawn (92) is devoted to recent developments in adsorption and the catalytic properties of metallic surfaces. Ries (93) has given an extensive account of the structure and sintering properties of a large number of important industrial catalysts.

In conclusion it may be said that substantial progress has been made in the last two years particularly in the direction of clarifying the thermodynamic aspects of adsorption and in elucidating the fundamental principles of catalytic action. Much of the progress towards determining the mechanism of catalytic reactions has been derived not only from the use of radioisotopes but also from the application of the mass spectrometer as a powerful tool for catalytic research.

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# PHOTOCHEMISTRY<sup>1</sup>

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In the present review, attention has been focussed mainly on photochemical kinetics in the gas phase. Particular attention has been paid to those investigations from which it is possible to derive quantitative information on the rates of elementary reactions involving atoms and radicals. At the same time, an attempt has been made to mention all photochemical papers appearing during the period under review with the exception of those concerned solely with organic synthesis under the action of light. Papers on photosynthesis and on the action of ionizing radiations have also been omitted since these subjects are dealt with elsewhere. Gas-phase reactions will be considered first.

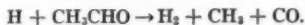
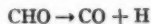
## ALDEHYDES

Brinton & Volman (1) have investigated the reaction of methyl radicals, produced by the pyrolysis of di-*t*-butyl peroxide with acetaldehyde. On the usual assumption that methane arises by



and ethane by recombination of methyls, they conclude that  $E_1 = 7.5$  kcal.,  $P_1 = 3.7 \times 10^{-2}$ . This is a very important result from the point of view of the mechanism of the acetaldehyde photolysis, since the value of the activation energy lies considerably below most previous estimates.

The photolysis of acetaldehyde in the presence of iodine has been re-investigated by Buchanan (2). The number of methyl radicals produced in the normal photolysis was assumed to be equal to the amount of  $\text{CH}_3\text{I}$  produced in the presence of iodine under comparable conditions. This was then compared with the amount of ethane formed in the absence of iodine. The amount of ethane formed was always considerably larger than that calculated from  $\phi_{\text{CH}_3\text{I}}$ . Buchanan suggests that this is due to additional methyl formed by the reactions



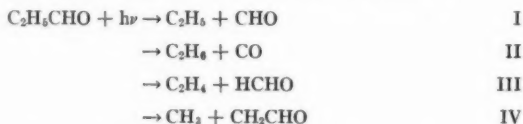
However, in view of the results on acetone-iodine mixtures discussed elsewhere in this review, it seems much more likely that the discrepancy is due to the deactivation of excited acetaldehyde molecules by iodine.  $\phi_{\text{CH}_3\text{I}}$  is therefore no measure of the rate of production of methyl radicals in the absence of iodine.

Dodd & Waldron (3) have concluded from analytical evidence that the

<sup>1</sup> The survey of the literature for this review was concluded in December, 1952.

chain terminating step in the high temperature photodecomposition of acetaldehyde is the combination of methyls to form ethane. They quote Danby, Buchanan & Henderson (4) as having reached the same conclusion.

One of the most important investigations in the period under review is that of Blacet & Pitts (5) on the photolysis of propionaldehyde, alone and in the presence of iodine. Limitations of space preclude a detailed discussion, and we will confine ourselves to a few of the more important results. The authors conclude that four separate primary processes are involved.



The most important evidence for these processes is: (a) The quantum yields in the presence of iodine of CO,  $C_2H_5I$ , and  $C_2H_6$  at 3130 Å were virtually constant and independent of temperature at 0.53, 0.45, and 0.02. The relatively large yield of ethyl iodide in a process independent of temperature is strong evidence for I. Also the virtual equivalence of  $\phi_{C_2H_5I}$  and  $\phi_{III}$  is strong evidence for the simultaneous formation of formyl radicals. (b) The temperature independence of ethane formation at 3130 Å in the presence of iodine indicates the importance of II. (c) The formation of a small amount of ethylene in the presence of iodine suggests the occurrence of III to a small extent. (d) The formation of a small amount of methane in the uninhibited photolysis is evidence for the occurrence to some degree of primary process IV.

Blacet & Pitts give a detailed discussion of the secondary reactions, based on a mechanism of a conventional type, but which is complex because of the large number of possible reactions of  $C_2H_5$ , CHO,  $CH_3$ , H, and  $C_2H_5CO$ . Their main conclusions are: (a)  $C_2H_5CO$  is unstable and there is no evidence of bipropionyl formation or of its participation in other reactions. This is in agreement with conclusions reached from the photolysis of diethyl ketone. (q.v.) (b) They arrive at a value of the activation energy of 13 kcal. for the decomposition of the formyl radical,



This is in good agreement with values obtained from work on other aldehydes. (c) For the reactions of ethyl radicals, they obtain the ratio

$$\frac{\phi_{\text{disproportionation}}}{\phi_{\text{combination}}} = 0.10.$$

In conclusion, they summarize the relative importance of primary processes I and II in Table I.

A brief investigation of the photolysis of propionaldehyde has also been made by Dodd (6) in which the reaction was followed by the rate of pressure

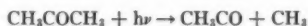
TABLE I  
RATIOS OF PRIMARY PROCESS II TO PRIMARY PROCESS I  
IN THE PHOTOLYSIS OF ALDEHYDES

Wave length Å	3,130	2,804	2,654	2,537	2,380
Energy, kcal./mole	91	102	108	113	120
Acetaldehyde	0.065	0.39	0.78	—	1.19
Propionaldehyde	0.046	0.24	1.19	1.32	—
n-butyraldehyde	0.049	0.39	0.89	1.06	—
iso-butyraldehyde	0.042	—	0.93	1.35	—

change. A pronounced curvature was found in the  $\log k$  vs.  $1/T$  plot. In view of the complex nature of the products, however, such a curvature is quite consistent with the results of the investigation of Blacet & Pitts. Dodd also investigated the reaction in intermittent light. The curve obtained was complex, and the processes occurring appear to be too complicated to permit this type of investigation of radical lifetimes.

#### KETONES

Pitts & Blacet (7) have re-investigated the photolysis of acetone-iodine mixtures. No ethane was detected in the presence of sufficient iodine, either at 3130 Å or at 2654 Å, and this seems conclusive evidence that the photolysis proceeds entirely by a free-radical mechanism. Only traces of methane were found, again indicating that iodine is a very efficient radical trap. The quantum yields of CO production varied somewhat with temperature and wave length, but were very small, the maximum value reported being 0.057. This indicates that even at the highest temperature employed (177°C.) the acetyl radical must possess some stability. One of the most interesting features of the work was the values of  $\phi_{\text{CH}_3\text{I}}$  and their variation with temperature and wave length. At 3130 Å  $\phi_{\text{CH}_3\text{I}}$  rose from 0.12 at 80°C. to 0.28 at 177°C. At 100°C. and 3130 Å it was 0.17, while at the same temperature and 2654 Å it was 0.50. This appears to confirm the prediction of Noyes & Dorfman (8) who suggested that iodine might deactivate excited acetone molecules. The low values of  $\phi_{\text{CH}_3\text{I}}$  are therefore no proof that the quantum yield of the process

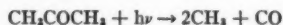


is less than unity in the absence of iodine.

Another recent investigation of the photolysis of acetone-iodine mixtures has been made by Martin & Sutton (89) using radioactive iodine to facilitate the analysis of the products of the reaction. Their results at 3130 Å are similar to those of Pitts & Blacet, and give very low values of  $\phi_{\text{CO}}$  at 100°C. (from 0.008 to 0.017), and low values of  $\phi_{\text{CH}_3\text{I}}$  which vary with conditions from 0.10 to 0.49. They explain their results in a similar way as attributable to a completely free-radical primary process, together with the quenching of

excited acetone molecules by iodine. They suggest that this may possibly occur by the formation of an acetone-iodine complex.

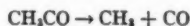
They also report a few experiments at 2537 Å, which are similar in nature. Their results suggest that the process



may not be involved, i.e., that it may be necessary to assume that some  $\text{CH}_3\text{CO}$  radicals dissociate in virtue of excess energy carried over from the primary step.

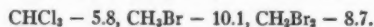
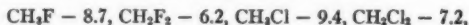
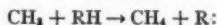
Another test of the free radical nature of the acetone photolysis has been made by Benson & Falterman (9) who photolyzed mixtures of  $\text{CH}_3\text{COCH}_3$  and  $\text{CD}_3\text{COCDD}_3$  using  $\lambda$  2537 Å at 60° C. and 120°C., and  $\lambda\lambda$  3000–3400 Å at 35°C. and 80°C. The products were then analyzed isotopically with a mass spectrometer. The isotopic distribution of the ethanes produced in the photolysis was found to correspond within 2 per cent under all conditions with that predicted by a completely free radical mechanism. They therefore conclude that the primary process in the acetone photolysis is a direct split into free radicals at all wavelengths.

A number of investigations have been made of the photolysis of mixtures of acetone and other substances. Volman & Graven (10) investigated acetone-butadiene mixtures. At 100°C., the addition of 438 mm. of butadiene to 26.5 mm. of acetone irradiated by the full light of a mercury arc, resulted in complete suppression of ethane formation. This is strong evidence for a completely free radical mechanism. It also indicates a very rapid addition of methyl radicals to butadiene. (No details are given in this preliminary report, and it may be inferred that methane formation is also completely inhibited.) The addition of butadiene also suppresses CO formation, suggesting that acetyl radicals also add to butadiene. By comparison of CO formation with acetyl addition, they conclude that the decomposition of the acetyl radical



has an activation energy of  $\sim 13.5$  kcal.

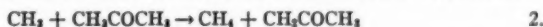
The photolysis of mixtures of acetone and a number of halogenated methanes has been investigated by Raal & Steacie (11). Interpreting the results in the usual way, by assuming that methane arises by hydrogen abstraction and ethane by methyl recombination, they obtain the following activation energies in kcal. for reactions of the type



The steric factors for the reactions are in the range  $10^{-2}$  to  $10^{-4}$ . In view of certain complications (which are being further investigated) when acetone

—CCl<sub>4</sub> mixtures are photolyzed, the quantitative aspects of the work should be taken with a certain amount of reserve. Kenyon (12) has made a similar investigation with acetone—*sec*-butyl chloride mixtures. HCl is a product, and he suggests that it arises from the decomposition of more complex products resulting from radical recombination. Under these circumstances, the attack of HCl by methyl radicals will complicate the reaction considerably.

Two investigations have been reported during the year in which acetone was photolyzed in the presence of hydrogen or deuterium or both. In the case of hydrogen, methane will be produced by two competitive processes



and ethane will be produced by recombination



From the rate of formation of methane and ethane, knowing the rate of reaction 2 from experiments on the photolysis of acetone alone, it is possible to arrive at values for  $k_3/k_4^{1/2}$ . Assuming that reaction 4 occurs at every collision, values of  $k_3$  can be obtained. In the case of acetone-deuterium mixtures reaction 2 is in competition with



and a determination of the CH<sub>3</sub>D/CH<sub>4</sub> ratio in the products gives the value of the ratio  $k_5/k_3$  and hence  $k_5$ . It is thus possible to arrive at the activation energies and steric factors of reactions 3 and 5, and similarly by the use of deutero-acetone, at the values for reactions 6 and 7.



By this method, Davison & Burton (13, 14) obtained the values

$$E_3 = 13.9 \text{ kcal.} \quad P_3 \sim 10^{-2}$$

$$E_5 = 14.3 \text{ kcal.} \quad P_5 \sim 10^{-2}.$$

They also photolysed acetaldehyde as a radical source and obtained values for  $E_3$  and  $E_5$  in approximate agreement.

In a similar investigation, Majury & Steacie (15) obtained the values

$$E_3 = 9.2 \text{ kcal.}$$

$$E_5 = 11.7 \text{ kcal.}$$

$$E_4 = 10.2 \text{ kcal.}$$

$$E_7 = 10.9 \text{ kcal.}$$

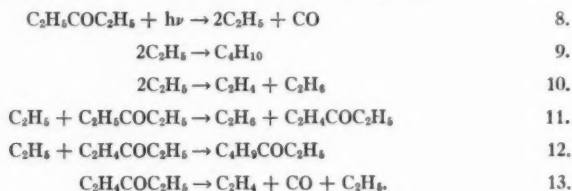
In a further paper (16) the cause of the discrepancy is discussed, and Majury



& Steacie conclude that the discrepancy is within the experimental error, and that the lower values are established.

Martin & Sutton (90) obtained results on the photolysis of methyl ethyl ketone in the presence of iodine which are very similar to those of Pitts & Blacet. They used radioactive iodine and carrier methods to determine the products. In the absence of iodine, the quantum yield of CO production was unity within the experimental error at 3130 Å and 120°C. In the presence of iodine CO, CH<sub>4</sub>, CH<sub>3</sub>I, and C<sub>2</sub>H<sub>5</sub>I were determined in the products. Some CH<sub>3</sub>COI was undoubtedly present, but the attempts to determine it were unsuccessful. The quantum yields of C<sub>2</sub>H<sub>5</sub>I are much higher than those of CH<sub>3</sub>I, confirming the relatively greater importance of the split to give C<sub>2</sub>H<sub>5</sub> and CH<sub>3</sub>CO, as compared with that to give CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>CO.

Considerable further work on the photolysis of diethyl ketone has been done in the period under review. Detailed investigations carried out in Rochester and in Ottawa have been reported in a joint paper by Kutschke, Wijnen & Steacie (17). The mechanism of the photolysis appears to be essentially similar to that of acetone, as suggested previously by Dorfman & Sheldon (18). The main differences are that the propionyl radical appears to be much less stable than acetyl, so that bipropionyl is not a product, ethyl radicals can disproportionate as well as recombine, and that the pentanonyl radical appears to be considerably less stable than the acetonyl radical. Kutschke *et al.* discuss their results in terms of the mechanism:



Their results lead to the values

$$E_{11} - \frac{1}{2}E_9 = 7.4 \text{ kcal.}$$

$$E_{10} \approx E_9 \approx 0$$

$$A_{10}/A_9 = 0.14$$

$$P_{11}/P_9^{1/2} \approx 10^{-3},$$

where the *A*'s represent the nonexponential factors, and the *P*'s the steric factors of the reactions.

Further work by Wijnen & Steacie (19) on the photolysis of partially deuterized diethyl ketone, CH<sub>3</sub>CD<sub>2</sub>COCD<sub>2</sub>CH<sub>3</sub>, gives confirmatory evidence for the above mechanism. In addition, the isotopic distribution of the ethane and ethylene formed indicates that the disproportionation of ethyl radicals occurs by a "head-to-tail" mechanism, i.e.,



Wijnen & Steacie (20) have also investigated the photolysis of mixtures of diethyl ketone and deuterium. In the presence of deuterium, the further reaction



also occurs. By comparing the rate of formation of  $\text{C}_2\text{H}_5\text{D}$  with that of  $\text{C}_2\text{H}_6$  over a range of temperature, they conclude that

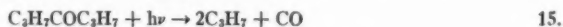
$$E_{14} - E_{11} = 5.9 \text{ kcal.},$$

whence

$$E_{14} = 13.3 \pm 0.5 \text{ kcal.}$$

The steric factor of reaction 14 works out at about  $10^{-3}$ .

The photolysis of di-*n*-propyl ketone has been investigated by Masson (21) using 3130 Å and covering a considerable range of temperature, pressure, and light intensity. The results are in agreement with the earlier postulation of two separate primary processes, i.e.,



The quantum yield of CO formation was virtually independent of pressure, temperature (up to 160°C.), and intensity, and this strongly suggests a very low stability for the radical  $\text{C}_3\text{H}_7\text{CO}$ . Reaction 16 can therefore be written as above, without the intermediate formation of  $\text{C}_3\text{H}_7\text{CO}$ . The sum of  $\phi_{\text{CO}}$  and  $\phi_{\text{C}_2\text{H}_4}$  in the low temperature range is only about 0.5, and it is suggested that the low value is due to some sort of internal degradation process. Secondary reactions are postulated which are analogous to those for diethyl ketone. Masson concludes that at 113°C., the ratio of disproportionation of propyls to recombination is about 0.2. The results lead to a value of 6.5 kcal. for  $E_{17} - \frac{1}{2}E_{18}$ , where



and to

$$P_{17}/P_{18}^{1/2} = 1.3 \times 10^{-4}.$$

The values are thus of the same order of magnitude as those for comparable methyl radical reactions. At higher temperatures, a chain reaction sets in, perhaps due to the occurrence of the reaction



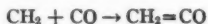
The author also estimates the activation energy of the decomposition of the propyl radical



to be approximately 20 to 21.5 kcal.

#### PHOTOLYSIS OF MISCELLANEOUS SUBSTANCES

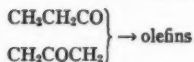
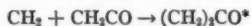
Kistiakowsky & Marshall (22) have made a further investigation of the photolysis of ketene, which casts considerable light on some of the doubtful points of the mechanism. By photolyzing a mixture of  $\text{C}^{13}\text{O}$  and ketene, and examining the infrared spectrum of the ketene remaining after the reaction, it was established that the reaction



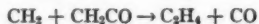
occurs readily, and in fact is five times faster under their experimental conditions than is the reaction



It had previously been suggested that the immediate product of the addition of methylene to ethylene is the trimethylene biradical. By the use of  $\text{CHD}=\text{CHD}$ , and an isotopic analysis of the resulting propylene, this suggestion was confirmed. They also found allene as one of the secondary products of the reaction. They suggest as the over-all mechanism:



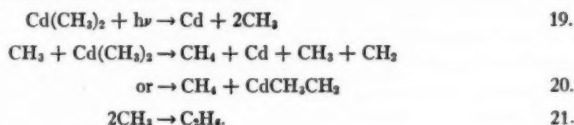
The photolysis of mixtures of ketene and methane with light of 2500 Å–3800 Å was found to result in the formation of carbon monoxide, ethylene, and ethane (23). The main reactions are reported to be



Work on "flash photolysis" has been continued by Knox, Norrish & Porter (24) who have investigated the photodecomposition of ketene by light of very high intensity produced by a flash discharge. At relatively low intensities or in the presence of a large excess of inert gas, they found the normal products of the photolysis, carbon monoxide and ethylene. At high intensities, owing to the very short duration of the flash and the large amount

of energy absorbed, the process is virtually adiabatic, and the gas is raised to a high temperature. As a result, the initial products are "cracked," the situation becomes very complex, and hydrogen, acetylene, and carbon are also formed. The authors were unsuccessful in an attempt to detect the methylene radical by absorption spectroscopy following the flash.

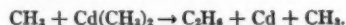
The photolysis of cadmium dimethyl has been investigated by Anderson & Taylor (25). Difficulties due to the deposition of cadmium on the window of the cell caused some experimental complications. The gaseous products of the photolysis were mainly methane and ethane, together with some ethylene, propane, and  $C_4$  hydrocarbons at the higher temperatures. The simplest explanation of the products is the mechanism:



A plot of  $\log [\text{CH}_4]/[\text{C}_2\text{H}_6]^{1/2}$  against  $1/T$  leads to

$$E_{20} - \frac{1}{2}E_{21} = 14 \pm 2 \text{ kcal.}$$

and hence to  $E_{20} = 14$  kcal. The increase in ethane production at high temperatures, however, necessitates a further source of methyl radicals, i.e., a chain step, and they suggest



The reaction mechanism is thus similar to that of mercury dimethyl. The activation energy of the abstraction reaction seems rather high by comparison with mercury dimethyl, however, and in view of the complications due to the deposition of cadmium metal on the cell, it is not certain that too much reliance should be placed on the exact value of  $E_{20}$ .

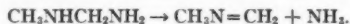
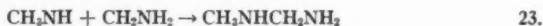
The authors also investigated the photolysis in the presence of hydrogen. In line with other photolyses which produce methyl radicals, the addition of hydrogen resulted in an increase in methane formation, presumably owing to the occurrence of the reaction.



From  $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}$  in the presence of hydrogen, they calculate  $E_{22} - \frac{1}{2}E_{21} = 13 \pm 2$  kcal. This result is only approximate, since no correction is applied for the methane formed by reaction 20. The value of  $13 \pm 2$  kcal. obtained for  $E_{22}$  appears to be somewhat high by comparison with other determinations, but the difference is probably within the experimental error.

Watson & Darwent (26) have reported briefly on the photolysis of methylamine. They conclude that the photolysis can be interpreted on the basis of the formation of the radicals  $\text{CH}_2\text{NH}_2$  and  $\text{CH}_3\text{NH}$ , either in the primary process or by subsequent hydrogen abstraction from methylamine. The

main products are hydrogen and a heavy compound ( $\text{CH}_3\text{N}=\text{CH}_2$ )<sub>3</sub>. They suggest that this is formed by the polymerization of  $\text{CH}_3\text{N}=\text{CH}_2$ , which is formed by the sequence



If this explanation is correct, reaction 23 must be much faster than either of the other possible recombination reactions. This is rather puzzling.

In a review paper (27), previous work on the photolysis of  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{CH}_2$ , and  $\text{N}_3\text{H}$  is discussed, and new data on the photolysis of  $\text{N}_3\text{H}$  is presented.

The gas phase photolysis of cyclo-octatetraene using a low pressure mercury arc is reported to lead to the formation of benzene and a non-condensable gas, probably acetylene (28).

The thermal and photochemical decomposition of  $\text{H}_2\text{O}_2$  vapor was studied by Stone & Taylor (29). A carrier gas was saturated with  $\text{H}_2\text{O}_2$  vapor and the mixture was passed through an irradiated quartz tube in a thermostat. This was done in order to minimize the thermal decomposition. The reactions of the OH radicals formed in the primary step with various carrier gases were studied. With CO, the formation of  $\text{CO}_2$  was found upon irradiation, and the following reactions are suggested:

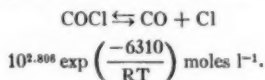


The amount of  $\text{CO}_2$  was greater than would be formed by the first reaction above, based on the estimated concentration of OH, and the second and third reactions are proposed. This was supported by the analyses of the condensates which indicate some regeneration of OH. With  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  as carriers, strong organic odors were obtained, indicating that reaction of OH with  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  had occurred, perhaps to form alkyl radicals and water. No organic products could be identified.

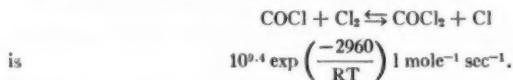
#### PHOTO HALOGENATIONS

Burns & Dainton (30) have studied the rate of photochemical formation of phosgene in continuous light as a function of light intensity, temperature, and composition of products. A thorough investigation was made of the effect of intermittent light, and the lifetimes of the radical chains under various conditions were evaluated. Corrections were applied for the non-uniformity of light absorption and for scattering and internal reflections. They found that the results are in better accord with the mechanism of Bodenstein than with that of Rollefson. The lifetime of the reaction chain did not show a dependence on the chlorine pressure as would be expected from the latter mechanism. The following constants were evaluated:

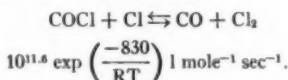
(a) the equilibrium constant  $k$  of the reaction



(b) the velocity constant of the reaction

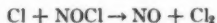


(c) the velocity constant of the reaction

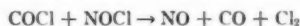


These values and the probable values of the velocity constants of the remaining two chain steps are shown to be consistent with the transition state theory. It is concluded from the results that the dissociation energy of the C-Cl link in phosgene is very much greater than in the COCl radical, and that the energy difference between the  $=\text{C}=\text{O}$  and  $^1\Sigma$  states of the CO molecule would be  $\sim 69$  kcal., provided that there is no change in the COCl group on separation from  $\text{COCl}_2$ .

In the second paper (31) these authors have studied the retarding effect of nitrosyl chloride on the photochemical formation of phosgene from CO and  $\text{Cl}_2$ . The rate constants and activation energies of the chain terminating steps



and



were measured.

The photochemical reaction between iodine monochloride and hydrogen has been investigated further by Wiig (32). The results are somewhat uncertain because of possible effects of moisture, adsorption, presence of impurities, etc. They are, however, quite consistent, and lend support to the mechanism previously proposed:



The quantum yield depends on the relative rates of reactions 25 and 27,

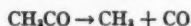
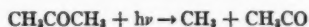
and for a value of  $[H]/[ICl] = 20$ , the quantum yield of HCl formation is about 0.038.

In a short note, Winning (33) suggests that the existence of methyl radicals, rather than hydrogen atoms, as the chain-carrying entity in the photochlorination of methane, is supported by the detection of formaldehyde rather than hydrogen peroxide in the chlorine-sensitized photo-oxidation of methane.

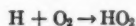
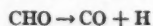
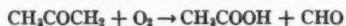
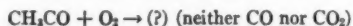
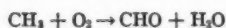
Rate equations are given for the photochlorination of toluene using light of 3600 Å by Miyazaki (34, 35).

#### PHOTO-OXIDATIONS

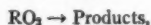
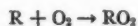
Marcotte & Noyes (36, 37) have investigated the photolysis of acetone-oxygen mixtures. This is essentially equivalent to an investigation of the reaction of methyl and acetyl radicals with oxygen. The reaction is very complex, and the mechanism is by no means established. It is, however, a very important piece of work, since it is a step in the direction of disentangling the elementary reactions involved in oxidation reactions. The mechanism appears to involve the normal steps in the acetone photolysis,



In view of the very rapid reaction of radicals with oxygen, ethane formation by recombination is completely suppressed. CO and CO<sub>2</sub> formation is therefore governed by oxidation reactions of radicals, which the authors formulate as



It seems probable that most of these reactions proceed by a mechanism of the type



and that the activation energy of the reactions is small.

The oxidation of propane induced by methyl radicals from azomethane was examined by Scheer & Taylor (38). They found that the products of the photo-induced reaction between 35°C. and 185°C. are condensables contain-



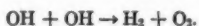
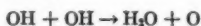
ing water and aldehydes, and the reaction is slow. Above 200°C. the photo-induced oxidation increases rapidly with temperature, and CO<sub>2</sub> and unsaturated hydrocarbons are detected among the products. Above 250°C. the azomethane decomposes thermally and produces a cool flame after an induction period. Below 185°C. the rate is independent of the total and partial pressures, is independent of temperature, and depends only on the azomethane. The authors suggest the oxidation of methyl radicals to methyl peroxide radicals, which rapidly change into methoxyl radicals which attack the propane to give methanol and propyl. The propyl and oxygen form propyl peroxide which can react with a methoxyl to form methanol, formaldehyde, and acetaldehyde. Above 250°C. the process probably involves the chain branching usually associated with peroxide breakdown.

The photochemical oxidation of monofluorodichloromethane sensitized by chlorine has been examined by Schumacher (39).

Norrish & Porter (40) have studied the reaction between hydrogen and oxygen initiated by flash photolysis using nitrogen dioxide as a sensitizer. The dependence of the explosion limits on various experimental parameters was determined. The reactions of the OH radical were followed by the intensity of its absorption spectrum, and the effects of hydrogen, oxygen, nitrogen, and water vapor on the intensity were examined. The propagation of the explosion resulting from the flash is shown to be mainly by binary collisions in the gas phase. The main reaction removing OH in the presence of hydrogen is



In the absence of hydrogen, at high temperatures, and at pressures up to 30 mm., OH is probably removed by



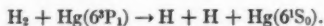
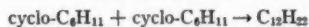
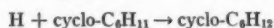
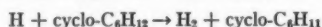
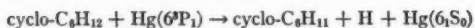
#### PHOTOSENSITIZED REACTIONS

Atkinson (41) investigated the mercury photosensitized reactions of tetrafluoroethylene at 30°C. The main products are hexafluorocyclopropane and polytetrafluoroethylene. The quantum yield of the reaction is low, and in view of the wide scatter of results, it is not possible to establish precise details of mechanism. He suggests a mechanism involving a primary split

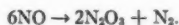


followed by addition reactions of CF<sub>2</sub>.

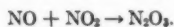
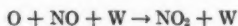
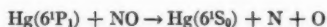
The reaction of methyl cyclopentane with photo-excited Hg(6<sup>3</sup>P<sub>1</sub>) atoms was shown to result (42) in the production of hydrogen, methyl cyclopentenes, and a heavy fraction with the formula C<sub>12</sub>H<sub>22</sub> which was considered to be mainly dimethyldicyclopentyls. The suggested mechanism is:



McGilvery & Winkler (43) have studied the photochemical decomposition of nitric oxide over a pressure range of 60 to 500 mm. using a low pressure mercury arc and a circulating system. At pressures of nitric oxide in excess of 50 mm., a good material balance was obtained in accordance with the over-all reaction



At a Hg pressure of  $1.7 \times 10^{-3}$  mm., the decomposition was shown to be photosensitized by  $\text{Hg}(6^1\text{P}_1)$  atoms, and the primary process was probably dissociation into nitrogen and oxygen atoms. The following mechanism is suggested:



A reduction in rate with added nitrogen is ascribed to deactivation of  $6^1\text{P}_1$  mercury atoms. When the mercury pressure was reduced to  $1 \times 10^{-3}$  mm., the reaction became a direct photolysis with an over-all quantum yield of 2.18 at  $\lambda$  1849 Å.

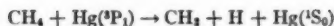
By the use of filters, it was shown that no photosensitization occurred with 2537 Å as found by Noyes (44) under conditions where 1849 Å radiation was presumed absent. The authors suggest that the reaction found by Noyes may have been due to  $7^3\text{S}_1$  atoms produced by stepwise radiation.

Darwent (45) has re-investigated the mercury photosensitized reaction of ethylene. The results are in general agreement with previous work in that they suggest the formation of an excited ethylene molecule in the primary act, which may be deactivated by collision. He concludes, however, that in addition excited ethylene molecules undergo deactivation at the wall.

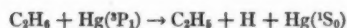
Agius & Darwent (46) have made a more precise investigation of the cadmium photosensitized reaction of propane.

Darwent & Hurtubise (47) have shown that metastable mercury atoms ( $6^3\text{P}_0$ ) are produced in the quenching of exciting mercury atoms ( $6^3\text{P}_1$ ) by various gases.

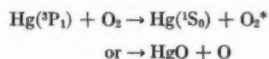
The mercury photosensitized oxidation of methane and ethane has been investigated by Gray (48) with the idea of confirming postulated oxidation mechanisms. He assumes that the primary processes are



and



and that these are followed by reactions of methyl and ethyl radicals with oxygen. However, the quenching cross section of oxygen is much greater than that of either methane or ethane. As a result, most of the quenching will be done by oxygen, and the main primary process is



Much work has been done on the mercury photosensitized formation of ozone, which appears to arise by



As a result, attack on hydrocarbons present may be due to  $\text{O}_2^*$ ,  $\text{O}_3$  and  $\text{O}$ , and the situation becomes complex.

Smith (49) finds that *cis*-butene-2 is not isomerized in the presence of excited sodium atoms ( $3^2\text{P}$ ).

Dubois & Noyes (50) have attempted to sensitize the decomposition of a number of compounds by means of benzene vapor. Positive results were obtained with methyl iodide, in which case the products were mainly  $\text{C}_2\text{H}_6$  and a little  $\text{CH}_4$ . Negative results were obtained in the case of hydrogen, oxygen, hydrogen chloride, nitrous oxide, methyl chloride, and methyl bromide. An attempt to photosensitize the decomposition of methyl iodide and methyl bromide with pyridine vapor was also negative.

#### MISCELLANEOUS GAS-PHASE INVESTIGATIONS

As mentioned in last year's review, the recombination of methyl radicals was investigated by two methods, and the results (51, 52) disagreed by a large factor. The value for the collision efficiency found by Miller & Steacie depended on a knowledge of the collision efficiency of the reaction



In view of the discrepancy between the results of Miller & Steacie and those of Gomer & Kistiakowsky, Durham & Steacie (53) have repeated the earlier work of Forsyth (54) on reaction 29. The reaction was investigated by the Paneth technique, using radioactive tellurium mirrors. A collision efficiency for reaction 29 of  $1.5 \times 10^{-4}$  was found, higher by a factor of 10 than Forsyth's value. With this value, the collision efficiency of methyl recombination



becomes 0.01 rather than  $4.4 \times 10^{-5}$  as calculated by Miller & Steacie, using Forsyth's value for reaction 29. Furthermore, it is pointed out that the

values for reaction 29 were determined at low pressures, and the collision efficiency in Miller & Steacie's work would be expected to be considerably higher. Durham & Steacie conclude, therefore, that there is no real discrepancy between their results and those of Gomer & Kistiakowsky, and that all work is compatible with a collision efficiency for reaction 30 at ordinary pressures, between 0.5 and 0.05.

The photopolymerization of acetylene with ultraviolet light leads to the formation of cyclo-octatetraene as reported by Kuri & Shida (55).

The photopolymerization of gaseous vinyl chloride in fused silica vessels was studied by Koizumi & Nakatsuka (56) who concluded that the lifetime of the chains was very short.

The spectrum of the  $\text{NH}_2$  radical has been obtained in absorption by Herzberg & Ramsay (57) in ammonia dissociated by flash photolysis (57). About 50 lines were obtained in the region 5700–6900 Å. This spectrum was shown to be identical with the  $\alpha$ -bands which are found in ammonia-oxygen flames and in discharges through streaming ammonia.

The absorption spectra of CH and NH radicals have been detected in acetylene-oxygen explosions by Norrish, Porter & Thrush (58). In addition, they find the Milliken and Swan bands of  $\text{C}_2$  and the three known systems of CH. With an excess of oxygen, they also detect a strong spectrum of OH.

The fluorescence of a number of substances of photochemical interest has been investigated. The substances investigated in the gas phase include acetone (59), formic acid (60, 61), phosgene (60), and methylene iodide (60, 61).

The reactions of ethyl radicals produced in various photochemical reactions have been reviewed by Ivin, Wijnen & Steacie (62).

Blacet (63) has given an excellent review of possible photochemical processes in the lower atmosphere, with particular reference to air pollution.

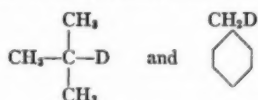
A review of the formation of photodimers by sunlight has been given (64) dealing mainly with those reactions leading to products of known constitution.

#### REACTIONS IN THE LIQUID AND SOLID STATE

Booth & Norrish (65) have investigated the products of the photolysis of a number of organic nitrogen compounds in solution in hydrocarbon solvents and in dioxane. The substances investigated included ammonia, *n*-hexylamine, ethyl methylamine, and a number of amides.

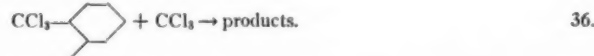
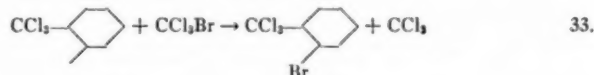
Bateman & Gee (66, 67) have investigated the photo-oxidation of ethyl linoleate, dihydromyrcene, octa-1-ene, digeranyl, gutta-percha (in *n*-decane solution), and rubber (in decalin containing cyclohexene hydroperoxide as a photosensitizer). The rate constants for the propagation and termination reactions were evaluated from the intercepts obtained by plotting the rate of oxygen absorption, which becomes constant shortly after the illumination is shut off. The rate constants measured in this way agree very well with the same constants evaluated by the sector method.

Brown & Russell (68) investigated the liquid phase photochlorination of 2-Methyl propane-2-d and of  $\alpha$ -d-toluene, i.e.,



In the photochlorination of the former compound, equal quantities of *t*-butyl chloride and of deuterium chloride were formed. There is thus no rearrangement of free radicals or hydrogen exchange between radicals and hydrocarbon during the photolysis. Similarly, the competitive photochlorination of d-toluene and cyclohexene gave no indication of exchange or rearrangement. The obvious explanation is that reaction of free radicals with chlorine is so rapid that exchange reactions and hydrogen abstraction by radicals are negligible.

The kinetics of the reaction between cyclohexene and trichloromethyl radicals produced by the photolysis of  $\text{CCl}_3\text{Br}$  with light of 3650 Å was studied by Melville, Robb & Tutton (69). The following mechanism is suggested:



The over-all progress of the reaction was followed by dilatometry under conditions where reaction 2 was rate determining and the rate was equal to  $k_{32} (I/2k_{34})^{1/2}$ . The value of  $I$  was determined by an inhibition technique, and the value of  $2k_{34}$  was measured using a rotating sector. The following values for the kinetic constants were obtained:

$$k_{32} (30^\circ\text{C}) = 2.56 \times 10^8 \text{ l mole}^{-1} \text{ sec}^{-1}$$

$$k_{32} (40^\circ\text{C}) = 3.08 \times 10^8 \text{ l mole}^{-1} \text{ sec}^{-1}$$

$$k_{32} (50^\circ\text{C}) = 3.65 \times 10^8 \text{ l mole}^{-1} \text{ sec}^{-1}$$

$$E \text{ (over-all)} = 3.4 \text{ kcal/mole}$$

$$E_{34} = \text{low}$$

$$A_{32} = 6.96 \times 10^5$$

$$A_{34} = 1.0 \times 10^6$$

In a later discussion (70) the authors submitted further values of the constants for the proposed kinetic steps:

$$k_{32} (30^\circ\text{C.}) = 1.3 \times 10^2 \text{ l mole}^{-1} \text{ sec}^{-1}$$

$$k_{32} (40^\circ\text{C.}) = 1.5 \times 10^2 \text{ l mole}^{-1} \text{ sec}^{-1}$$

$$k_{34} (50^\circ\text{C.}) = 1.90 \times 10^2 \text{ l mole}^{-1} \text{ sec}^{-1}$$

$$E (\text{over-all}) = E_{33} - \frac{1}{2}E_{35} = 4.5 \text{ kcal./mole}$$

$$2k_{35} = 2.0 \times 10^7 \text{ l mole}^{-1} \text{ sec}^{-1}$$

$$2k_{36} = 2.5 \times 10^8 \text{ l mole}^{-1} \text{ sec}^{-1}$$

No activation energy for the termination step could be detected, although the method should be able to detect 3 or 4 kcal.

The photo-degradation of polymethylmethacrylate to monomer in light of 2537 Å was shown to be true depolymerization, having an over-all quantum efficiency in excess of  $10^2$  (71). In a second paper (72), the authors measured the rates of initiation, propagation, and termination for this reaction, the former from retardation and molecular weight experiments, the latter two using the rotating sector method. The termination reaction was found to be abnormally slow, and is probably diffusion-controlled.

The photochlorination of benzene using 4630 Å at 25°C., 35°C., and 45°C. was found to be a chain reaction in the absence of oxygen and to be autocatalytic (73).

The photochemical chlorination of a number of compounds has been examined by Pieck & Jungers (74) and the quantum yields were measured for  $\text{C}_6\text{H}_6$ ,  $\text{o-C}_6\text{H}_4\text{Cl}_2$ , toluene, xylene,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , 1,2-dichloroethane, thiophene, naphthalene, cyclohexene, methyl cyclohexene, decahydronaphthalene,  $\text{C}_6\text{H}_5\text{Cl}$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ , tetrahydrobenzene, and ethyl benzene. A number of paraffins examined reacted too rapidly to measure, with quantum yields in excess of  $10^5$ . The photochlorination of fatty acids and their derivatives is described in a second paper (75).

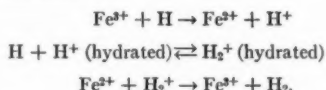
Dainton & James (76) have investigated photochemical electron transfer with special reference to the formation of hydrogen atoms in aqueous solution.

Brealey & Uri (77) showed that  $\text{FeCl}_4^-$  acts as a photocatalyst for the oxidation of alcohol by thionine.

It has been shown (78) that the quartz ultraviolet irradiation of ferrous ions in aqueous solution in the absence of oxygen leads to the formation of ferric salt and molecular hydrogen. The primary absorption of a light quantum forms an excited ion  $(\text{Fe}^{2+} \cdot \text{H}_2\text{O})^*$  which can then be either deactivated or dissociated according to



Subsequent possible reactions are



The kinetics of decomposition of potassium ferrocyanide in aqueous solution in the presence of air, oxygen, and nitrogen was investigated (79) by following the course of the reaction by the change in the pH. Oxygen was found to have no influence on the rate, and it is concluded that the reaction is



A mechanism of photo-reaction and reverse thermal reaction is given. In the light, the process has a negative temperature coefficient due to the action of the reverse reaction, which is effectively that of  $\text{Fe}(\text{CN})_6\cdot\text{H}_2\text{O}^{3-}$  with cyanide ion, and which has an activation energy of about 24 kcal./mole.

Uri (80) has published a comprehensive review of reactions involving inorganic free radicals in solution, covering the literature from 1930 to July, 1951. A section of this review covers the photochemical formation of atoms and free radicals in solution and their subsequent reactions.

The photochemical decomposition of solid nitrates has been shown to produce nitrite and oxygen using a high pressure mercury arc (81). The quantum yields vary from 0.002 for lithium nitrate to 0.19 for cesium nitrate in the order  $\text{LiNO}_3$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{AgNO}_3$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{La}(\text{NO}_3)_3$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{KNO}_3$ ,  $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ , and  $\text{CsNO}_3$ , which is the order of the polarization properties of the cations. The rates are almost independent of the temperature in the range 30°C. to 250°C.

The photodecomposition of barium azide was studied by Thomas & Tompkins (82), who present a mechanism for the process in terms of the production of free electrons which are trapped at deep surface traps.

#### TECHNIQUE

A number of investigations have been made which are of interest from the point of view of technique. Thus Heidt & Boyles (83) have investigated the effect of operating conditions on the output of  $\lambda 2537$  from a low-pressure mercury arc, and Christie & Porter (84) have studied uranyl oxalate actinometry at the very high light intensities prevailing in flash photolysis, and have also investigated the output from flash-discharge lamps.

A valuable method of actinometry applicable to low intensities of ultra-violet (less than  $10^{13}$  quanta/sec.) has been described by Calvert & Rechen (85). They have removed the limitations to the general use of malachite green leucocyanide by an improved method of preparation and purification of the leucocyanide and have confirmed the quantum yield data of Harris *et al.* (86) by two independent methods. Their results indicate that the



quantum yield of dye formation is 1.00 at all wavelengths employed (2537 Å, 2654 Å, 2804 Å, and 3130 Å). At intensities above  $3 \times 10^{13}$  quanta/sec. incident on an area of 0.3 cm.<sup>2</sup>, an apparent reduction in quantum yield was found, owing to the strong absorption by the product dye.

A mathematical analysis of the effect of the wall on photochemically induced chain reactions has been made by Noyes (87). He discusses the situation in which a second order reaction is accompanied by a first order wall reaction and derives an expression for the wall effect.

Gomer has derived expressions (88) for the nonsteady state distribution of radicals due to diffusion in the case of a first order gas and a first or second order wall reaction. The effect of expansion and longitudinal diffusion on radical concentrations in flow systems is discussed, and expressions giving the magnitude of the effects are given. It is shown that in fast flow systems expansion may simulate a first order reaction.

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# PHYSICAL PROPERTIES OF HIGH POLYMERS<sup>1</sup>

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## INTRODUCTION

Reviews on high polymers in previous volumes of this series have covered specialized topics: the effect of oxygen on physical and chemical properties (1), copolymerization (2), thermodynamics of solutions (3), and polymeric electrolytes (4). The present review deals with certain physical properties of polymers: mechanical, electrical, and optical [excluding light scattering, which has been comprehensively treated in two recent publications (5, 6)]. The period covered is roughly from 1949 through 1952.

Two important treatises which antedate this period slightly should be mentioned, that on mechanical behavior of polymers by Alfrey (7) and that on rubberlike elasticity by Treloar (8). Also, the *Proceedings of the First International Rheological Congress* (9) contains a variety of short papers on mechanical properties. The *Proceedings of the Second International Congress on Rheology* (10) had not yet appeared when this review was prepared.

## VISCOSITY

*Intrinsic viscosity.*—Following the treatment of Flory & Fox (11, 12, 13), intrinsic viscosity measurements can now be used to estimate the dimensions of linear polymer molecules in solution (the root mean square end-to-end chain length,  $(\bar{r}^2)^{1/2}$ , for example); to separate the effects of solvent interaction and long-range spatial interference from those of local steric hindrance and bond structure in increasing the value of  $(\bar{r}^2)^{1/2}$  over that to be expected for a random coil with free rotation; and to estimate the values of thermodynamic parameters  $\psi_1$  and  $\kappa_1$  related to the entropy and heat of mixing of polymer with solvent. These calculations have been applied by Flory & associates to polyisobutylene (14, 15), polystyrene (16), natural rubber (17), gutta percha (17), polymethyl methacrylate (18), cellulose tributyrate (19), cellulose tricaprylate (19), and polydimethyl siloxane (20), using a variety of solvents. Additional studies on polystyrene have been made by Cragg, Dumitru & Simkins (21).

In the Flory-Fox procedure, the value of the root mean square end-to-end length in the absence of solvent and long-range interactions,  $(\bar{r}_0^2)^{1/2}$ , is first derived from the intrinsic viscosity in a poor solvent at the critical consolute temperature, making use of a universal hydrodynamic constant  $\Phi$  which should be the same for all polymers. The constant  $\Phi$  is dimensionless and, if  $[\eta]$  is expressed in deciliter/gm., its order of magnitude should be  $10^{-2}$

<sup>1</sup> The survey of the literature pertaining to this review was concluded in December, 1952.

times Avogadro's number; it has been determined experimentally by combining intrinsic viscosity and light scattering data for polyisobutylene and polystyrene to be  $2.1 \times 10^{21}$ , as compared with the value of  $3.6 \times 10^{21}$  derived from the theory of Kirkwood & Riseman (22) in the limit of high molecular weight. The value of  $(\bar{r}_0^2)^{1/2}$  is found to be independent of the nature of the solvent employed, proportional to the square root of the molecular weight (as specified by the theory), and somewhat dependent on temperature; it decreases slightly with increasing temperature for the synthetic polymers, more rapidly for the cellulose esters, and negligibly for natural rubber. The value of  $(\bar{r}_0^2)^{1/2}$  is greater than that calculated on the basis of free rotation by a factor which ranges from 1.4–1.7 for rubber, gutta percha, and polydimethyl siloxanes to 2.7 for cellulose tributyrate. These factors represent the effects of local interference with free rotation in expanding the polymer coil. They confirm the expectation of easy rotation in natural rubber and siloxanes, but not the earlier impressions of a rodlike configuration in cellulose derivatives; at the temperatures of measurement, the latter are only moderately more extended than the synthetic polymers.

The value of  $(\bar{r}^2)^{1/2}$  exceeds that of  $(\bar{r}_0^2)^{1/2}$  by a factor  $\alpha$  which varies from unity in a poor solvent at the critical consolute temperature to something like 1.5 for a good solvent such as cyclohexane for polyisobutylene or benzene for polystyrene. In a good solvent,  $\alpha$  varies little with temperature; in a poor solvent, it increases with increasing temperature.

An alternative theoretical approach, related to those of Debye & Bueche (23) and Kirkwood & Riseman (22), in which a variable degree of solvent immobilization within the polymer coil is considered, has been followed by Peterlin (24) and Kuhn & Kuhn (25, 26), and discussed by Riseman & Eirich (27). The theory of Kirkwood & Riseman and related calculations have been applied to experimental measurements on polystyrene solutions (28) and on wire models of molecular coils (29).

The dependence of apparent intrinsic viscosity on velocity gradient was studied by Fox, Fox & Flory (30), who found that in polyisobutylene solutions the logarithm of the specific viscosity decreased linearly with the rate of shear (except for a polymer of extremely high molecular weight). The rate of decrease was independent of concentration (at low concentrations), and proportional to the square of the intrinsic viscosity when the same polymer was compared in different solvents. Theoretical calculations by Kuhn & Kuhn (31) and Peterlin (32) predict a different dependence on velocity gradient ( $\dot{\gamma}$ ); according to both these treatments, the apparent specific viscosity should decrease linearly with  $\dot{\gamma}^2$ . A very strong dependence of apparent specific viscosity on velocity gradient was found in moderately dilute solutions of sodium thymonucleate by Katz & Ferry (33).

Experimental techniques in the measurement of intrinsic viscosity have been critically reviewed by Elliott & Davis (34). New determinations of the dependence of intrinsic viscosity on molecular weight include those of Pepper (35, 36) on polystyrene, Baysal & Tobolsky (37) on polymethyl methacry-

late, Johnson & Wolfangel (38) on polybutadiene, and Philipp & Bjork (39) on cellulose acetate. Measurements on intrinsic viscosities of polystyrene, polymethyl methacrylate, and a methyl methacrylate-styrene copolymer in many different solvents by Alfrey, Goldberg & Price (40) showed that the effect of solvent depends not only on its cohesive energy density but also on electron donation-acceptance relationships (cf. Spurlin (41)). Viscosities of dilute solutions of nitrocellulose were studied by Moore (42) and Lindsley (43). Viscosities of mixtures of two polymers in dilute solution were studied by Krigbaum & Wall (44).

Kuhn, Kuhn & Buchner (45) have given an extensive review of the hydrodynamic behavior of macromolecules in dilute solution, which summarizes the results of many theoretical papers.

*Concentration dependence of viscosity in dilute solution.*—The equation of Huggins (46),  $\eta = \eta_0(1 + [\eta]c + k'[\eta]^2c^2 + \dots)$ , where  $\eta$  and  $\eta_0$  are the viscosities of solution and solvent,  $[\eta]$  the intrinsic viscosity, and  $c$  the concentration, has been discussed in numerous papers. Simha (47) derived it for a dumbbell shaped solute molecule and concluded that the coefficient  $k'$  should be independent of molecular size but should depend on the shape. Eirich & Riseman (48) discussed the dependence of  $k'$  on molecular shape and solvent environment. Riseman & Ullman (49), following the methods of Kirkwood & Riseman (22), have calculated the value of  $k'$  for molecular shapes of dumbbell, rod, and centrosymmetric flexible coil, obtaining 11/15 and 3/5, respectively, for the latter two. A much simpler approach by Brinkman (50), deriving the differential effect on viscosity of adding a spherical solute molecule to a suspension of such molecules considered as a continuum, provides the value of 0.7.

Extensive experimental measurements of  $k'$  have been made by Alfrey, Goldberg & Price (40) on polystyrene, polymethyl methacrylate, and a methacrylate-styrene copolymer, and by Streeter & Boyer (51) on polystyrene in many different solvents. For polymethyl methacrylate (40),  $k'$  ranged from 0.3 in the best solvents to 1.4 in the poorest. For polystyrene (51),  $k'$  ranged from 0.22 in the best solvent to 0.60 in the poorest; in comparing values in 14 solvents,  $k'$  decreased monotonically with increasing  $[\eta]$ , and (with two exceptions)  $k'[\eta]^2$  was found to be a linear function of  $[\eta]$ , a relation predicted by Eirich & Riseman (48).

*Viscosity of concentrated solutions.*—The dependence of viscosity on concentration in concentrated solutions can be formulated only empirically, and as in the past many equations have been employed in recent work. The Martin equation, in which the logarithm of the reduced specific viscosity is a linear function of concentration, was successfully applied to polystyrene in many solvents over the concentration range from 2 to 12 gm./deciliter by Spencer & Williams (52), Streeter & Boyer (51), and Weissberg, Simha, & Rothman (53); also by Bestul & Belcher (54) for GR-S rubber in *o*-dichlorobenzene. Doolittle (55) has employed the relation  $\ln \eta = \alpha \exp(-K/c^{1/4}) + \gamma$ , where  $c$  is weight concentration. Johnson *et al.* (56) found viscosity propor-

tional to  $c^5$  (here  $c$  is concentration in weight polymer per unit volume of solution) for polyisobutylene in several solvents from  $c=3$  to  $c=20$  to 40 gm./deciliter; a similar relation was noted by DeWitt & Morrison (57). Other measurements of viscosities of concentrated solutions have been those on polyvinyl acetate by Ferry *et al.* (58), on polystyrene by Jenckel & Rehage (59), on GR-S by Bestul and co-workers (60), and on polyisobutylene and polystyrene by Eirich & Newman (61).

The dependence of viscosity on molecular weight and choice of solvent has been combined empirically with the concentration dependence by use of reduced variables. The reduced specific viscosities of polystyrenes of different molecular weights, plotted by Weissberg, Simha, & Rothman against the product of the concentration and the intrinsic viscosity, gave curves which fell fairly close together (53). The relative viscosities of polyvinyl acetate in several different solvents, plotted by Ferry and associates against the volume concentration, gave curves which fell fairly close together (58). Finally, the relative viscosities of polyisobutylene solutions in which both molecular weight and choice of solvent were varied, plotted against the product of concentration and molecular weight to the 0.68 power, gave a single curve (56). Thus, roughly, a change in molecular weight changes the effective concentration scale, while a change in solvent changes the magnitude of the viscosity of the solution in proportion to the viscosity of the solvent.

The temperature dependence of viscosity in concentrated solutions is usually expressed by the apparent activation energy for viscous flow, even though this is itself somewhat temperature-dependent (56). At a given temperature, the apparent activation energy for solutions of polyisobutylene and polyvinyl acetate increases linearly with concentration over a considerable range, though not necessarily extrapolating into the correct value for the solvent at zero concentration (56, 58); it increases only very slightly with increasing molecular weight (56, 58).

All the above statements regarding concentrated solutions apply to low shearing stresses where deviations from Newtonian flow are negligible; this condition is ordinarily met with the falling sphere method or with capillary viscosimeters under low pressure. At higher stresses, the dependence of the apparent viscosity on shearing stress has been followed in coaxial cylinder viscosimeters by Eirich & Newman (61) and Schremp, Ferry & Evans (62); and in capillary devices by Bestul (54, 60). It can be expressed in the form  $\eta_a = \eta/f(\mathfrak{T}/G_a)$ , where  $\eta_a$  is the apparent viscosity at shear stress  $\mathfrak{T}$ , and  $G_a$  is a constant with the dimensions of stress which is usually interpreted as an internal modulus of rigidity. The function  $f$  may be simply  $1 + \mathfrak{T}/G_a$  (54, 61, 63) or a more complicated expression (60, 62). The parameter  $G_a$  is practically independent of temperature (61, 62, 63); at moderate concentrations it is roughly proportional to concentration (62, 63), though over wider concentration ranges it varies in a complicated manner (54).

*Viscosity of undiluted polymers.* —The dependence of apparent viscosity



on shearing stress in undiluted polymers (above the glass transition, of course) is quite similar to that in concentrated solutions. The function  $f(\mathfrak{I}/G_a)$  has been represented as  $1 + \mathfrak{I}/G_a$  in polyisobutylenes of low molecular weight by Leaderman and associates (64), as a series  $1 + \mathfrak{I}/G_a$  plus terms up to  $(\mathfrak{I}/G_a)^4$  in polystyrenes by Spencer & Dillon (65), and as  $(G_a/\mathfrak{I}) \sinh (\mathfrak{I}/G_a)$  in polymethyl methacrylate by Whitfield & Baron (66). The latter form has also been applied to concentrated solutions (62). Other relations involving fractional powers of the stress have also been employed (67, 68). The parameter  $G_a$  is practically independent of temperature (65) and roughly inversely proportional to the molecular weight (from 86,000 to 700,000) for polystyrene (69). Its significance as an internal modulus of rigidity reflecting orientation of chain segments in steady-state flow is supported by theoretical calculations of Spencer (69). In contrast to the marked non-Newtonian behavior of these linear addition polymers, phenolic resins were found by Dienes (70) to exhibit Newtonian flow even when their viscosities were very large. Such resins were converted to viscoelastic bodies by a small degree of cross-linking, however (71).

The viscosity extrapolated to zero shear stress, or measured under conditions of low stress where non-Newtonian deviations could be neglected, was determined as a function of temperature and molecular weight for polyisobutylene and polystyrene by Fox & Flory (72, 73, 74). Additional measurements have been reported by Leaderman (64) on polyisobutylenes of low molecular weight and by Ferry, Grandine & Fitzgerald (75) on one of high molecular weight. The temperature dependence resembles that of concentrated solutions in that the apparent activation energy for viscous flow is itself temperature-dependent; in fact, the logarithm of the viscosity is a linear function not of  $1/T$  but of  $1/T^2$  for polyisobutylene and of  $1/T^3$  for polystyrene. The apparent activation energy is practically independent of molecular weight except for very low values of the latter (for polystyrene,  $M_n < 25,000$ ). The decrease in activation energy with decreasing molecular weight in the low range is attributed by Fox & Flory (74) to an increase in free volume with increasing number of chain ends; this is also reflected in the dependence of glass transition temperature on molecular weight (74).

While the effect of molecular weight on the temperature dependence of viscosity is determined by the number-average and is slight, the effect of molecular weight on the viscosity itself at constant temperature is determined by the weight average and is very great. In polyisobutylene and polystyrene, the viscosity is proportional to the 3.4 power of the molecular weight for  $M \geq 17,000$  and  $\geq 30,000$  respectively (72, 73, 74). At lower molecular weights the dependence is less; this is presumably connected with the fact that at lower molecular weights the temperature variation of the viscosity becomes molecular weight dependent. The exponent 3.4 also expresses the dependence of relative viscosity on molecular weight in polyisobutylene solutions at constant concentration (56).

Other investigations of viscosity of undiluted polymers include those of

Buchdahl & Nielsen on polystyrene (76, 77, 78) and of McLaren *et al.* on polyvinyl acetate and several other substances (79).

#### EQUILIBRIUM ELASTICITY

*Theory of rubberlike elasticity.*—James & Guth (80) have given a new presentation of their network theory. Wall & Flory (81) have analyzed the differences between their theories and that of James & Guth. The quantitative predictions of rubberlike elasticity theory were well confirmed by the experiments of Flory, Rabjohn & Shaffer (82) on the elasticity of rubbers vulcanized with disazodicarboxylates, in which the degree of cross-linking was known from chemical evidence. Other papers on the statistical theory of elasticity include those of Ishihara & associates (83 to 86).

*General homogeneous strain and large strains.*—An extension of the classical theory of elasticity to large strains in a solid of negligible compressibility had been advanced by Mooney (87) before the development of the statistical network theory of rubberlike elasticity. Rivlin (88, 89) has elaborated a general theory to account for finite strains which predicts relations between different types of superimposed deformations; for example, a tube, when twisted, elongates and contracts laterally unless constrained. This theory has been quite well confirmed by experiments by Rivlin & Saunders (90) and Gent & Rivlin (91, 92, 93), in which rubber tubes were subjected to simultaneous tension, torsion, and inflation, prisms were subjected to simultaneous tension and torsion, tubes were turned inside out, etc. Other experiments with superimposed deformations have been reported by Treloar (94), who subjected sheets of rubber to biaxial stress, and Boonstra (95), who stretched and inflated tubes at quite large strains. Finite strains have also been treated theoretically by Oldroyd (96).

Related phenomena appear in the steady-state flow of viscoelastic liquids, where stresses appear normal as well as tangential to the direction of laminar flow, as shown by experiments of Weissenberg (97), Garner, Nissan & Wood (98), Greensmith & Rivlin (99), and DeWitt and associates (100). This "normal stress effect", also, has been treated theoretically by Rivlin (101, 102) and by Mooney (103).

*Theory of reinforcement.*—The effect of carbon black and other particulate fillers on the elastic modulus of rubber has been treated theoretically by Bueche (104), who postulates that points on rubber molecules are bonded to filler particles and that the segments between such points act as additional network strands. The increase in modulus then depends on the ratio  $f/r$ , where  $f$  is the number of adherence points per unit surface area and  $r$  the particle radius. The dependence of modulus on volume fraction of filler as measured in neoprene-carbon stocks follows the form predicted by the theory, and the area  $1/f$  is found to be of the order of  $5 \text{ \AA}^2$ . That there is indeed very strong binding between carbon and unsaturated polymer molecules, resembling primary chemical bonds, is inferred from the experiments of Stearns & Johnson (105) and Zapp & Guth (106). Schmidt (107) has reported

that fillers other than carbon reinforce GR-S if the particle size is sufficiently small. In another theoretical approach, Rehner (108) has calculated the energy of mixing of polymer with filler, which is regarded as a negative measure of reinforcement. It contains a positive term related to expansion of the polymer and a negative term related to surface energy; for active fillers, the latter predominates.

*Miscellaneous.*—Other investigations of equilibrium elastic properties include those of Merz, Nielsen & Buchdahl on the molecular weight dependence of mechanical properties of polystyrene (109, 110); of Mooney & Wolstenholme on the difficulty of measuring the modulus near the glass transition temperature (111); and of Carey, Shulz & Dienes on the mechanical properties of polyethylene (112).

#### TIME-DEPENDENT MECHANICAL PROPERTIES

A state of mechanical equilibrium, like one of chemical equilibrium, must always be qualified as existing only with respect to certain processes. Equilibrium elasticity of lightly vulcanized rubbers can be discussed, as above, because a time scale can be chosen within which the system is very nearly in equilibrium with respect to configurational changes of network strands but not at all in equilibrium with respect to degradative reactions which break or rearrange crosslinks.<sup>2</sup> Closer examination, however, may reveal that even under optimum conditions no exact mechanical equilibrium can be attained. Nonequilibrium mechanical properties in cases of marked time-dependent phenomena are currently of particular interest.

*General phenomenology of viscoelastic materials.*—Many polymers and polymer solutions conform in the limit of small stresses to the definition of a linear viscoelastic material, whose mechanical behavior can be represented by some combination of Hookean elastic and Newtonian viscous elements. Its mechanical properties can be represented by any of several functions, including creep, stress relaxation, real or imaginary part of the complex dynamic elastic modulus, distribution function of relaxation times or of retardation times, etc. (7, 113, 114). Many of the relations among these functions have been derived in exact form by Gross (115, 116, 117). Such relations have been further discussed by Sips (118), who treats also the cases of creep recovery, extension under constant rate of strain, etc.

Because of the difficulty of numerical evaluation of the exact equations, approximate methods have been sought to derive the distribution function of relaxation times from stress relaxation or complex dynamic modulus data. What amounts to a zero order approximation has been given by ter Haar (119, 120, 121). A first approximation has been used by Alfrey (7), Nolle (122), Guth *et al.* (123), and Ferry and associates (124); equivalent approxi-

<sup>2</sup> To cite a chemical analogy, in the system of hydrogen, oxygen, and liquid water at room temperature, it is easy to choose a time scale within which the system is in equilibrium with respect to the dissolution of the gases in the water but not at all with respect to the reaction  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ .

mations have been discussed by Schwarzl (125, 126). Second approximation methods have been given and applied to experimental data by Ferry & Williams (127, 128) and Andrews (129, 130). A theory of higher order approximations of a different sort has been developed by Schwarzl & Staverman (131). When dynamic modulus data are used to derive a distribution function, the calculation can be made from both real and imaginary parts to provide an experimental check (124, 127). The same approximation methods can be used to calculate the distribution function of retardation times from creep or complex dynamic compliance data (128). A method for interconversion from stress relaxation to the real part of the dynamic modulus, in which the distribution function enters only as a second order correction, has been given by Marvin (132).

The behavior of viscoelastic materials in various types of strain has been treated by Read (133) and Sips (134). The propagation of elastic waves through such materials has been treated by Adler, Sawyer & Ferry (135), Sips (136), and Astbury (137). The behavior of viscoelastic materials in oscillating deformations in certain types of apparatus with cylindrical symmetry has been treated by Markovitz (138).

A uniform terminology and notation appropriate to the above phenomenological approach has been proposed by Leaderman (139, 140). To imitate the mechanical properties of a system with a small number of relaxation times, an electrical analogue has been suggested by Stambaugh (141). The mechanical behavior of an idealized viscoelastic system (with, in effect, two relaxation times) under various types of deformation has been treated by Oldroyd (142, 143). Buchdahl & Nielsen (144) have discussed an entirely different approach to viscoelastic behavior involving fractional powers of stress and time.

*Experimental methods.*—Marked improvements have been introduced in methods for measuring time-dependent mechanical properties. Some of these have been reviewed by Ferry, Sawyer & Ashworth (145), Eirich (146), and Marvin (147).

For stress relaxation, Tobolsky and associates have used automatic recording stress balances (148, 149) and differential transformer devices (150, 151, 152). Watson, Kennedy & Armstrong (153) have described an apparatus for measuring stress relaxation in very short time intervals. For creep measurements, Dahlquist, Hendricks & Taylor (154) have used a special device to provide constant stress. Hastewell & Ritson (155) have described a concentric cylinder device for applying constant torque to a viscoelastic liquid.

In dynamic (sinusoidally time-dependent) measurements, most methods provide both real and imaginary parts of the complex dynamic elastic modulus. For very low frequencies, Philippoff (156) employs differential transformers for simultaneous measurement of stress and strain in shear. At moderately low frequencies Nolle (157) has used a rocking beam oscillator, and DeWitt and associates use a torsional method in which changes in stress and strain are followed by electromagnetic devices (158). The latter is applicable to liquids (defined roughly as viscoelastic materials which cannot

support their own weight within the duration of an experiment) as well as solids. Another torsional apparatus for liquids is described by Oldroyd, Strawbridge & Toms (159); this does not measure phase differences. In the audiofrequency range, the complex modulus is obtained from propagation of longitudinal waves in solids by Nolle (157) and Hillier & Kolsky (160), and of transverse waves in liquids by Ferry & associates (135); and from measurements of electrical impedance in electromagnetic transducers, in liquids by Smith, Ferry & Schremp (161), and in solids by Fitzgerald & Ferry (162), Marvin, Fitzgerald & Ferry (163), and Marvin & Weiss (164). Other methods which fall in the audiofrequency range but do not provide a continuous range of frequencies are the vibrating reeds of Nolle (157) and Nielsen, Buchdahl & Leveault (165), the torsion pendulums of Nielsen for solids (166) and Sittel, Rouse & Bailey for liquids of low viscosity (167), and the tuning fork device of Rorden & Grieco (168). In the range from  $10^4$  to  $10^6$  c.p.s., torsional crystals have been introduced by Mason (169) and used by Baker, Mason & Heiss (170) and by Rouse, Sittel & Bailey (171) for viscoelastic liquids; a modification of this method has been described by McSkimin (172). Magnetostrictive devices have been used on solids by Nolle (157) and on liquids by Rich & Roth (173). Finally, in the megacycle range, Mason and associates have determined the complex shear modulus of liquids from measurements of reflection of shear waves at the surface of a piezoelectric crystal (174, 170).

Most of the above dynamic methods deal with deformation in shear, but some with elongation (157, 160, 165) or compression (157). The latter types of deformation involve changes not only in shape but also in volume, which are, however, negligible except under such conditions of frequency and temperature that the shear modulus approaches the bulk modulus in order of magnitude. By propagating longitudinal waves in the megacycle range ("bulk" waves), as carried out by Nolle & Mowry (175), Ivey, Mrowca & Guth (123), Mason and associates (176), and Nolle & Sieck (177), information can be obtained concerning the complex bulk modulus, though for quantitative results the data must be combined with shear data at the same frequencies.

*Dilute Solutions.*—Baker, Mason & Heiss (170) have measured the complex shear modulus<sup>3</sup> in solutions of polyisobutylene, polypropylene, polyethylene, polystyrene, natural rubber, and polybutadiene microgel in the concentration range from 0.1 to 1 gm. per deciliter. For liquids, the complex modulus is often written  $G^* = G' + i\omega\eta'$ , where  $G'$  and  $\eta'$  ( $\eta' = G''/\omega$ ) are the real parts of the complex shear modulus and complex dynamic viscosity, respectively.<sup>3</sup> In these dilute solutions, both  $\eta'$  and  $G'$  are, of course, frequency-dependent. With decreasing frequency,  $\eta'$  approaches the steady

<sup>3</sup> Instead of using the complex shear modulus,  $G' + i\omega\eta'$ , Baker, Mason & Heiss express data mostly in terms of three frequency-dependent parameters,  $\eta_A$ ,  $\eta_B$ , and  $\mu_B$ . Here  $\eta_A$  is almost equal to the solvent viscosity,  $\eta_0$ ; to the approximation that it is exactly the solvent viscosity, the other two are related to  $G'$  and  $\eta'$  by the following complex reciprocal:  $G' + i\omega(\eta' - \eta_0) = 1/(1/\mu_B - i/\omega\eta_B)$ .

flow viscosity of the solution and  $G'$  approaches 0; with increasing frequency,  $\eta'$  approaches the solvent viscosity,  $\eta_0$ , and  $G'$  increases progressively. Data were obtained at 20, 40, and 80 kc. with a few results at 2.3 kc. and about 15 mc. Although the form of the frequency dependence cannot be well specified with so few points, three separate dispersion regions have been inferred, and identified with possible molecular elastic mechanisms, as discussed in detail by Baker & Heiss (178). Rouse & Sittel (179) have applied the same piezoelectric technique between  $10^4$  and  $10^6$  c.p.s. to dilute solutions of polystyrene and polyisobutylene, and have added measurements at 0.22, 0.9, and 2.3 kc. with their hollow torsion pendulum (167). At constant frequency,  $G'$  and  $\eta' - \eta_0$  increase with concentration, somewhat faster than directly proportional; and  $G'$  decreases with increasing temperature, at least in good solvents (170). In a poor solvent,  $G'$  is smaller, and its temperature variation may be less or even in the opposite direction. Whenever dispersion is present, however, it is difficult to interpret changes in dynamic properties with concentration or temperature at constant frequency (180).

The basic theory for dynamic mechanical properties of dilute solutions has been provided by Kirkwood (181), who showed that for oscillating deformations whose frequencies are near the rotational diffusion constants of solute molecules (moving either as a whole or by segments), the rate of strain will be out of phase with the stress and the viscosity will be complex; i.e., a rigidity appears, and both viscosity and rigidity are frequency-dependent. Explicit calculations by Kirkwood & Auer (182) for the case of thin rigid rods at infinite dilution predict a Maxwellian dispersion in which  $G'$  rises from zero to  $3RTc/5M$  ( $c$  concentration in gm./cc.,  $M$  molecular weight) and  $\eta' - \eta_0$  drops from the steady flow viscosity increment to one-fourth that value. The relaxation time is proportional to the solvent viscosity and approximately to the cube of the length of the solute molecule. An extension by Fraenkel (183) employs as a model a dumbbell with two masses connected by a spring; the predicted dispersion of  $\eta' - \eta_0$  involves a rotational relaxation time as in the theory of Kirkwood & Auer plus a vibrational relaxation time. Cerf (184) has calculated the frequency dependence of  $\eta' - \eta_0$  for a dilute solution of rigid ellipsoids of revolution. None of these models is adequate to represent a real polymer molecule, however, with the possible exception that the rod of Kirkwood & Auer resembles nucleic acid and their theory predicts the correct order of magnitude of  $G'$  in moderately dilute solution (33).

Using a different approach, Cerf (185) has considered a dilute polymer solution as equivalent to a dilute suspension of viscoelastic spheres. Following the treatment of ordinary liquid droplets by Taylor (186), the complex viscosity of the dilute solution can be related to the complex viscosity of the viscoelastic droplet; from experimental data, frequency-dependent viscosity and shear elasticity coefficients are then derived for the molecule (which is probably roughly equivalent, in this respect, to a droplet of concentrated polymer solution).

Finally, Rouse (187) has developed a theory which takes into account relaxation processes in a randomly coiled flexible molecule, by diffusion of segments of various lengths. This theory predicts the dispersion of dynamic rigidity and viscosity from knowledge of the steady flow solution viscosity, the solvent viscosity, and the molecular weight, no other parameters being needed. It shows remarkably successful agreement with the rather sparse data available (179).

*Undiluted polymers of low molecular weight.*—Next simplest to consider after dilute solutions, in which the polymer molecules are more or less isolated, is the time-dependent mechanical behavior of undiluted polymers; here the molecules are entangled, but the concentration as a variable is absent. Polymers of low molecular weight (e.g., less than 10,000) have the advantage that the range of time scale necessary for a complete description is somewhat less broad than for high molecular weights.

Leaderman and associates (64) have measured shear creep curves of polyisobutylenes of low molecular weight over a wide range of temperatures, using a coaxial cylinder apparatus. Harper, Markovitz & DeWitt (188) have measured both parts of the complex dynamic rigidity,  $G' + i\omega\eta'$ , for a polyisobutylene of molecular weight about 6000 and a silicone oil of molecular weight about 60,000, over a range of frequencies from 10 to 100 c.p.s. and of temperatures from  $-50^\circ$  to  $+60^\circ$ . At low frequencies and high temperatures,  $\eta'$  approached the steady flow viscosity,  $\eta$ , and  $G'$  was as small as 100 dyne/cm<sup>2</sup>; at high frequencies and low temperatures,  $\eta'$  was considerably less than  $\eta$ , and  $G'$  was as high as  $10^7$  dyne/cm<sup>2</sup>. The interrelation of time, frequency, and temperature in these and other investigations is discussed further below. Hoff (189) detected existence of complex viscosity, and hence time-dependent mechanical effects, in polyethylene melts, at a frequency in the neighborhood of 20 c.p.s.

Using much higher frequencies, Mason, Baker, McSkimin, & Heiss (174, 176, 190) have measured the complex rigidities of polyisobutylenes of molecular weights from about 900 to 5600 and of a poly- $\alpha$ -methyl styrene. At 10 mc. and  $25^\circ\text{C}$ .,  $G'$  was of the order of  $10^9$  to  $10^{10}$  dyne/cm<sup>2</sup>. The increase in  $G'$  and decrease in  $\eta'$  with increasing frequency are described by several frequency-independent parameters representing shear elasticities and viscosities. All of these parameters decrease with increasing temperature, and appear to change exponentially with  $1/T$ . There is also dispersion of longitudinal waves (176); for very low molecular weights, this appears to be primarily a result of shear relaxation processes, but at higher molecular weights a bulk relaxation also contributes.

*High molecular weight polymers: stress relaxation and creep.*—Stress relaxation in tension was measured in polyisobutylenes of molecular weight from 0.6 to 1.4 million, over a temperature range from 30 to  $100^\circ\text{C}$ ., by Andrews, Hofman-Bang & Tobolsky (149). The shape of the relaxation curve was independent of elongation at low elongations, and independent of temperature and molecular weight (when time was plotted logarithmically). The



latter variables profoundly influenced the position on the logarithmic time axis, however. Similar measurements were made between  $0^{\circ}$  and  $-70^{\circ}\text{C}$ . by Brown & Tobolsky (191). At the lowest temperatures, the decay of stress was more abrupt and was independent of molecular weight and even of the presence of cross-links, since butyl rubber behaved much like polyisobutylene. McLoughlin & Tobolsky (192) measured stress relaxation in polymethyl methacrylate from  $40^{\circ}$  to  $135^{\circ}\text{C}$ ., covering a range of consistencies from soft and rubbery to hard and glasslike; similar measurements on GR-S from  $-33^{\circ}$  to  $-64^{\circ}\text{C}$ . have been reported by Bischoff, Catsiff & Tobolsky (151). At a glasslike consistency, the rate of relaxation depends on thermal history (192, 193).

Creep measurements in elongation at constant stress for polyisobutylene and GR-S over a wide range of temperatures (194), as well as for several other polymers (154), have been made by Dahlquist & associates, and on polyisobutylene in shear by Van Holde & Williams (195). Tensile creep of polyvinyl chloride plastics has been measured by Dyson (196), and on this and several other polymers by Tobolsky, Alfrey and associates (197 to 200). Creep in compression of several polymers at elevated temperatures has been reported by Dienes (201). Mooney & Wolstenholme (111) studied creep in torsion of several rubbers at low temperatures, finding complications which were attributed to slow crystallization processes.

*High molecular weight polymers: dynamic properties.*—Nolle (122) determined the real and imaginary parts of the complex Young's modulus on a natural rubber vulcanizate and a carbon-filled buna-N vulcanizate at frequencies between 0.1 c.p.s. and 120 kc. and temperatures between  $-60^{\circ}$  and  $100^{\circ}\text{C}$ ., using a variety of methods. The real part of the modulus,  $E'$ , ranged from  $2 \times 10^7$  to  $2 \times 10^{10}$ , increasing with increasing frequency and decreasing temperature; the loss tangent  $E''/E'$  ranged from 0.01 to the order of unity, and usually passed through a maximum with changing temperature or frequency. This was the first investigation to cover a wide enough range of these variables to provide at least an approximate picture of the dispersion of mechanical properties in a polymer. Narrower regions of frequency and temperature have been covered by Witte, Mrowca & Guth (202) on butyl rubber and GR-S vulcanizates, by Ferry and associates (163, 203, 204) on polyisobutylene, and by Hopkins (205) on a variety of soft polymers. More recently, the real and imaginary parts of the complex shear modulus have been obtained between 25 and 5000 cycles and between  $-40$  and  $140^{\circ}\text{C}$ ., with both temperatures and frequencies closely spaced to determine the shape of the dispersion in detail, by Fitzgerald & Ferry on two compositions of polyvinyl chloride and dimethyl thianthrene (162), by Grandine & Ferry on polystyrene (206), and by Fitzgerald, Grandine, & Ferry on polyisobutylene (207). With increasing frequency or decreasing temperature, again,  $G'$  rises from values characteristic of a soft rubber to values characteristic of a hard glass.

Measurements of longitudinal wave propagation have been made by

Nolle & associates (175, 177) between 2 and 30 mc. over a range of temperatures, on a buna-N vulcanizate and several other rubbers. At these high frequencies, the results are partly determined by the complex bulk modulus, and the latter can be obtained by combining data on longitudinal and shear wave propagation. The imaginary component of the complex bulk modulus appeared to be small. Similar measurements were made on natural rubber and butyl rubber vulcanizates by Ivey, Mrowca & Guth (123).

All the above-quoted investigations of dynamic properties involved small amplitudes of deformation such that both components of the complex dynamic modulus were essentially independent of amplitude. Dynamic measurements at higher amplitudes have been made by Fletcher & Gent (208) and Gui, Wilkinson & Gehman (209) on rubbers, and by Sauer, Marin & Hsiao on polystyrene (210). In unloaded rubbers, both components of the complex modulus decrease somewhat with increasing amplitude; in loaded rubbers, these effects are much magnified, and the imaginary component may vary in a complicated manner.

*Interrelation of time, frequency, and temperature; composite plotting methods.*—Tobolsky and associates (149, 151, 191, 192) found that, for several polymers, stress relaxation curves plotted as stress/strain against log time at various temperatures could be superposed by sliding along the log time axis to construct a composite curve. Ferry (180, 203) showed that similar superpositions could be predicted for dynamic measurements by assuming that whatever the distribution of relaxation times all of them have the same temperature dependence, and that the magnitudes of the elastic mechanisms associated with the relaxation times are proportional to the absolute temperature and the density. In this case the reduced variables  $G'T_0\rho_0/T\rho$  and  $G''T_0\rho_0/T\rho$  should superpose at all temperatures when plotted against  $\omega a_T$  (or its logarithm), where  $a_T$  is the factor expressing the ratio of any relaxation time at  $T$  to that at the reference temperature  $T_0$ . This prediction has been confirmed for several polymer systems (75, 163, 203, 204, 206, 211), the value of  $a_T$  being chosen to make both  $G'$  and  $G''$  superpose. According to the above assumptions,  $a_T$  should be obtainable also from the temperature dependence of the steady flow viscosity as  $\eta\rho_0T_0/\eta_0\rho T$ . This has been quite well confirmed for polyisobutylene (75, 203) and polystyrene (206); however, the most critical test (75), extending over a very wide range of temperatures, showed that the values of  $a_T$  from viscosity agreed with those from superposition of stress relaxation data but were slightly lower than those from superposition of dynamic data. The corresponding reduced variables for creep have been given by Dahlquist & Hatfield (194) and applied to polyisobutylene. The factor  $T_0/T$  has sometimes been used (149) in reducing stress relaxation data; the factor  $\rho_0/\rho$ , which is never far from unity, has usually been omitted. Under conditions where  $G'$  approaches values characteristic of a hard glass, a slightly more complicated treatment modifies the factor  $T_0/T$  (211).

Alternative composite plotting methods have involved assuming a spe-

cific functional form for the temperature dependence of  $a_T$ , usually exponential in  $1/T$ , as employed by Harper, Markovitz & DeWitt (188) and Dahlquist & Hatfield (194); or even a functional form for the dependence of the measured mechanical property on both temperature and time, as employed by Conant, Hall & Lyons (212). Over large temperature ranges, however,  $a_T$ , like the steady flow viscosity, is far from being exponential in  $1/T$ . An entirely different composite plot was used by Mason and associates (176), who found that for low molecular polyisobutylene the shear elasticity (a derived frequency-independent parameter) was a function of density alone at different molecular weights and temperatures. Interrelations between time, frequency, and temperature have also been discussed by Müller (213) and Schwarzl & Staverman (214).

The temperature dependence of  $a_T$  provides an instructive approach to the temperature dependence of all time-dependent mechanical properties.<sup>4</sup> The use of an entirely arbitrary reference temperature is avoided either by substituting for  $a_T$  the time (or reciprocal frequency) which corresponds to a characteristic feature of the mechanical behavior, as done by Bischoff, Catsiff & Tobolsky (151), or by calculating the apparent activation energy of all relaxation processes,  $\Delta H_a = d \ln a_T / d(1/T)$ , which has been done from both stress relaxation (151, 192, 215) and dynamic data (75, 206, 211). With decreasing temperature nearing the glass transition,  $\Delta H_a$  attains large values, of the order of 50 to 100 kcal./mole. Its rise is gradual for polyisobutylene and sharper for polystyrene and plasticized polyvinyl chloride (216); for polymethyl methacrylate and GR-S, it appears to be sharper still, and  $\Delta H_a$  goes through a maximum (151, 192). These changes, like those in the apparent activation energy of viscous flow, are probably associated with changes in free volume (74).

*Analysis of time dependence.*—A composite curve obtained with reduced variables as described above predicts the time (or frequency) dependence over a wide range at the reference temperature. Both transient and dynamic data can be converted to the distribution function of relaxation times (127, 129). For a polyisobutylene of viscosity-average molecular weight 1.35 million, distributed by R. S. Marvin of the National Bureau of Standards to various cooperating laboratories, excellent agreement between transient and dynamic data is obtained in this manner (75, 215). This confirms both the experimental data and, for this polymer at least, the assumption that  $a_T$  is very nearly the same over a very wide range of relaxation times. The logarithmic distribution function<sup>5</sup> for polyisobutylene has a peculiar bimodal

<sup>4</sup> Tobolsky (215) denotes this quantity by  $\kappa$  when derived from superposition of time-dependent mechanical data, and by  $a_T$  when derived from the steady flow viscosity.

<sup>5</sup> The distribution of contributions of Young's modulus in the range of relaxation times  $d\tau$  is written as  $E$  by Andrews (129) and  $D$  by Tobolsky (192). The logarithmic distribution in the range  $d \log_{10} \tau$  is written as  $E'$  and  $D'$  respectively. The logarithmic distribution of contributions to the shear modulus in the range  $d \ln \tau$  is written as  $K$  by Alfrey (7) and  $\Phi$  by Ferry (124). When Poisson's ratio is close to  $1/2$ ,  $D' = 6.91\Phi$ .

shape (75); in the short-time region it is practically independent of molecular weight (75, 163, 188, 215), but in the long-time region it depends profoundly on molecular weight and probably on molecular weight distribution (215). Tobolsky found that the long and short time regions could be approximately represented by a box (149, 217, 218, 219) and a wedge (220) respectively, permitting calculation of time-dependent properties from the distribution function by analytical rather than graphical (204) methods. In certain regions of time scale, however, this procedure gives only the correct order of magnitude (75).

The relaxation distribution function has been determined in the short-time range for several other polymers from stress relaxation (151, 192) and dynamic data (206, 211). Here its shape appears to be independent not only of molecular weight but also, approximately, of the chemical composition of the polymer (216), though some differences in steepness are apparent (151). No attempt has been made to describe the shape analytically; however, the first derivative of the stress relaxation function, which is closely related to the distribution function, has been fitted by Tobolsky & associates to a Gaussian error curve (151).

Qualitatively the relaxation distribution function is understood to be associated with rates of configurational change in molecular segments of varying lengths. Kuhn (221) has discussed the relation of such lengths to the apparent viscosity encountered by a tiny particle moving through the tangled molecules, a viscosity which has also been measured by Schachman & Harrington in solutions of nucleic acid (222). The shape of the distribution function has been calculated theoretically by Blizard (223) on the basis of viscous coupling of individual elastic mechanisms to the "average medium." Both this theory and that of Rouse (187), which is intended of course only for very dilute solutions, predict that at high frequencies the logarithmic distribution should be given by  $\Phi = k\tau^{-1/2}$ . The experimental distributions in undiluted polymers show segments in the short-time region which over a time scale of several powers of 10 correspond roughly to an equation of this form with exponents between  $-0.5$  and  $-0.9$  (216).

*Concentrated solutions.*—For systems intermediate between very dilute solutions and undiluted polymer there is, of course, an increase in both real and imaginary parts of the complex elastic modulus with increasing concentration. The concentration dependence at constant frequency (or time) is difficult to analyze, because effects of concentration and time are intermingled. In the general range from 5 to 50 per cent polymer, however, a simple analysis similar to that of temperature dependence can be made by using reduced variables (180). Assuming that all relaxation times have the same concentration dependence, and that the magnitudes of the elastic mechanisms associated with them are proportional to concentration,  $c$ , the reduced variables  $G'T_0/Tc$  and  $\eta'/\eta$  should superpose when plotted against  $\omega\eta T_0/Tc$ . Here, by using the steady flow viscosity  $\eta$ , the need for empirical parameters like  $\sigma_T$  is eliminated. The reference state is a hypothetical one of unit concentration and unit viscosity. This treatment, and an

analogous one for stress relaxation (62), have been successfully applied to concentrated solutions of polyvinyl acetate (124, 224), polyisobutylene (62, 180, 203, 225), and polystyrene (62, 206).

From dynamic and transient measurements combined in this manner, the relaxation distribution functions have been obtained for concentrated solutions of polystyrene (206) and several polyvinyl acetates (124, 127) and polyisobutylenes (203, 226). They are similar in shape to that of an undiluted polymer; the shape in the long time region is markedly influenced by molecular weight and molecular weight distribution.

*Miscellaneous.*—Less extended series of data have been presented in numerous other investigations of time-dependent mechanical properties. Dynamic measurements at moderately low frequencies have been made on rubbers by Enabnit & Gehman (227), Waring (228), Nielsen, Buchdahl & Claver (229), and Davies (230); on plastics by Müller (231), Nielsen, Buchdahl & Levreault (165), and Kawai and associates (232, 233, 234); and on films and filaments by Horio and associates (235) and Dunell & Dillon (236). Measurements in the megacycle range have been made on various polymers by Protzman (237), Natta & Baccaredda (238), and Melchor & Petrauskas (239). Polycrystalline polymers such as polyethylene have been studied by both transient (199, 240) and dynamic (178) methods, but the results are of course more difficult to interpret than those for polymers which are primarily amorphous.

Other investigations of a more practical nature which are more or less directly concerned with time-dependent mechanical properties include those on friction by Lincoln (241), Schallamach (242), and Shooter & Tabor (243); on cracking and crazing by Carey (244), DeCoste, Malm & Wallder (245), and Hsiao & Sauer (246); on tack by Voet & Geffken (247); on extrusion and molding by Dexter & Dienes (248) and Spencer & Gilmore (249); on tensile strength by Flory, Rabjohn & Shaffer (250) and Boyer (251); and on the mechanism of brittle fracture by Taylor (252).

#### ELECTRICAL PROPERTIES

There have been comparatively few recent investigations of electrical properties of polymers as detailed as those of a decade or more ago by Fuoss (253) and Baker (254).

*Dilute solutions.*—Debye & Bueche (255) have calculated the effect of hindered rotation in modifying the average dipole moment of an isolated polymer coil, and illustrated it with a few measurements on poly-*p*-chlorostyrene at a frequency below the dispersion region. This subject was also treated theoretically by Kuhn (256). An extensive series of measurements of the complex dielectric constant,  $\epsilon' - i\epsilon''$ , of dilute solutions of polyvinyl chloride in tetrahydrofuran was made by de Brouckère & Van Nechel (257), covering a range of frequencies from 0.5 to 3.5 mc., of temperatures from  $-35$  to  $-10^{\circ}\text{C.}$ , and of concentrations from 1 to 8 gm./deciliter. The

shape of the dispersion corresponded to a value of 0.7 for the distribution parameter  $\alpha$  of Fuoss & Kirkwood (258), which is actually higher than the value of 0.53 predicted by the theory of Kirkwood & Fuoss (259); previous results on much more concentrated systems had always given lower values, corresponding to broader distributions. As expected, the maximum value of  $\epsilon'$  increased and the dispersion region was shifted to lower frequencies with decreasing temperature and with increasing concentration. In such a rather dilute solution, the apparent energy of activation for the relaxation processes, as calculated from temperature shift of the loss maximum, was closer to the apparent energy of activation for viscous flow of the solvent than that of the solution. Some dielectric measurements of 3 per cent cellulose nitrate solutions in acetone have been reported by Scherer & Testerman (260) in the frequency range from 0.1 to 0.5 mc. A dispersion in two steps of surprising sharpness was observed. The dielectric constants of solutions of polyvinyl acetate in benzene-hexane mixtures have been measured by Yoshioka (261).

*Undiluted polymers.*—The complex dielectric constant of polyethylene terephthalate, both crystalline and amorphous, has been determined by Reddish (262) over a range of frequencies from  $100$  to  $10^7$  c.p.s. and of temperature from  $-80^\circ$  to  $180^\circ\text{C}$ . Two regions of dispersion were observed, one at high temperatures attributed to dipole rotation, and one at low temperatures attributed to some process involving hydroxyl groups. The latter is associated with a much lower apparent activation energy. Both mechanisms appear to operate only in the amorphous regions. Additional loss at very high temperatures and low frequencies is attributed to conductance processes. The complex dielectric constant of polyvinyl chloride was measured by Girard, Abadie & Charbonnière (263) over a range of frequency from  $25$  to  $10^6$  c.p.s. and of temperature from  $18^\circ$  to  $125^\circ\text{C}$ .; and by Fitzgerald & Miller (264) from  $15$  to  $10^4$  c.p.s. and  $-50^\circ$  to  $140^\circ\text{C}$ . In both these investigations, the region of dispersion was found to shift to higher frequencies with increased temperature. Other studies on dielectric properties include those of Okada on polyamides (265) and Shaw & Windle on films and fibers at very high frequencies (266). The specific resistance and power factor of polystyrene have been measured by Matheson & Caldecourt (267).

*Concentrated solutions, gels, and plastics.*—Würstlin (268) reported loss tangents,  $\epsilon''/\epsilon'$ , at  $10$  mc. at various temperatures for solutions of polyvinyl acetate in benzyl benzoate, as well as polyvinyl chloride in tricresyl phosphate, ranging from pure solvent to pure polymer. Plots of loss tangent against temperature showed a single peak in polymer-rich and in solvent-rich compositions, and a suggestion of two peaks in the center of the concentration range. Schallamach & Thirion (269) measured loss tangents in rubbers swollen by polar solvents, between frequencies of  $0.1$  and  $40$  mc. and  $-180^\circ$  and  $70^\circ\text{C}$ . Here the frequency dispersion showed two peaks. Fitzgerald & Miller (264) measured both components of the complex dielectric constant in mixtures of polyvinyl chloride and dimethyl thianthrene

over a wide range of temperatures from 15 to 10,000 c.p.s., as well as in similar systems of polyvinyl chloride with several other plasticizers (270), the concentration ranging in each case from pure solvent to pure polymer. Both real and imaginary components showed the temperature dispersion (represented by a single peak for the loss tangent) shifting progressively to higher temperatures with increasing polymer concentration. The apparent activation energy for the relaxation processes passed through a minimum with increasing concentration. Dyson (271) reported shifts in loss factor maximum with temperature for various compositions of polyvinyl chloride in tricresyl phosphate and dioctyl phthalate ranging from 26 per cent to 46 per cent polymer by weight; the frequency and temperature ranges were from 0.8 to 1500 kc. and 10 to 120°C. respectively. Dielectric measurements on various polyvinyl chloride compositions at a single frequency (1000 c.p.s.) over a range of temperatures have been reported by Nielsen, Buchdahl & Levreault (165). Other measurements on polyvinyl chloride in dioctyl phthalate have been reported by Girard, Abadie & Charbonnière (272).

*Analysis of temperature and frequency effects.*—By assuming that all electrical relaxation times have the same temperature dependence, as in the mechanical case, and that the magnitudes of the polarizations are proportional to density and inversely proportional to absolute temperature, reduced variables can be introduced which should superpose at all temperatures and frequencies when plotted against  $\omega b_T$ , where  $b_T$  is the ratio of any relaxation time at the experimental temperature to that at a chosen reference temperature (211). Ferry & Fitzgerald have applied this treatment to the data of Fitzgerald & Miller (270) on two compositions of polyvinyl chloride and dimethyl thianthrene, and found the temperature dependence of mechanical and electrical relaxation times (as represented by  $a_T$  and  $b_T$ ) to be identical (211). The apparent energies of activation for the two relaxation processes are therefore identical, but both are strongly dependent on temperature, as described above for the mechanical case. This method of reduced variables has also been applied (273) to older data of Fuoss (253).

From a composite curve of either  $\epsilon'$  or  $\epsilon''$  obtained with reduced variables, a distribution function of electrical relaxation times can be calculated by the same second approximation methods used for mechanical data (128). The resulting distributions are molecularly analogous to mechanical distributions of retardation times, as obtained from creep or complex compliance data with the same approximations (128). The electrical relaxation and mechanical retardation distributions have been compared for two compositions of polyvinyl chloride and dimethyl thianthrene (211); the electrical distributions are much broader. This difference has been attributed by Ferry & Fitzgerald to the minor effect of differences in segment length on the electrical distribution, in contrast to a profound influence of the assortment of apparent segment lengths on the mechanical properties (211).

Other discussions of the relations between electrical and mechanical



relaxation processes have been given by Würstlin (274, 275), Müller (276), and Scheele & Timm (277).

#### OPTICAL PROPERTIES

*Flow birefringence.*—A comprehensive review by Cerf & Scheraga (278) on the theory and application of flow birefringence in dilute polymer solutions has very recently appeared. It is unnecessary to discuss this subject here, therefore, except to add a few additional references by Signer & Liechti (279) on solutions of nitrocellulose and by Joly (280, 281) on the effects of polydispersity and interaction.

The flow birefringence of concentrated solutions has not been extensively investigated, though it is of considerable interest for correlation with the interpretation of time-dependent mechanical properties. Signer & Schmidli (282) have studied two samples of polystyrene at concentrations up to 20 gm./deciliter and two of cellulose nitrate up to 5 gm./deciliter; the extinction angle and birefringence were found to vary in a complicated manner with velocity gradient and concentration. Bourgoïn & Joly (283) studied the flow birefringence of gelatin solutions under conditions approaching gelation. Conner & Donnelly (284) measured flow birefringence of viscose solutions at a concentration of 7 per cent, as well as the disappearance of birefringence after cessation of flow. The latter process, surprisingly, appeared to be characterized by a single relaxation time.

An effect related to flow birefringence is that of acoustic birefringence. Its application to polymer solutions has been discussed by Peterlin (285).

*Electrical birefringence.*—Applications of electrical (as well as magnetic) birefringence to polymers have been discussed by Stuart & Peterlin (286). This phenomenon has been successfully exploited by Benoit (287 to 290) in dilute solutions of thymonucleic acid and tobacco mosaic virus. His method provides for either a sinusoidally alternating potential or an interrupted potential of very short duration, and from analysis of the change of birefringence with time the rotary diffusion constants are calculated.

*Stress birefringence.*—The term "stress birefringence" literally includes flow birefringence, of course, but as applied to undiluted polymers or plasticized compositions it usually denotes double refraction associated with elastic deformation under more or less equilibrium conditions or else with stresses which are slowly relaxing. The extensive work of Treloar (8) on equilibrium stress birefringence antedates the period of this review. Stein & Tobolsky (291) have discussed at length the interpretation of simultaneous measurements of birefringence relaxation and stress relaxation, in terms of various molecular processes such as configurational rotatory diffusion, chain scission by chemical reaction, growth of crystals, and orientation of crystals. From such measurements on vulcanized and unvulcanized rubbers, polyamides, plasticized polyvinyl chloride compositions, and polyethylene (197, 198, 199) deductions were made concerning the relative contributions of

these processes to relaxation at various temperatures. More recently, stress birefringence has been reviewed by Stuart (292); the birefringence of rubber at large equilibrium deformations has been treated theoretically by Isihara and associates (293); and measurements of stress birefringence in polyethylene from 20° to 90°C. have been reported by Crawford & Kolsky (294) and interpreted in terms of crystallite orientation.

*Miscellaneous.*—Measurements of the refractive index of natural rubber at different wavelengths have been reported by Wood & Tilton (295). Wiley, Brauer, & associates have measured the refractive indices of a number of polymers (296) including rubbers (297, 298), polyvinyl chloride and polystyrene (299, 300), and various acrylate and methacrylate polymers (301). Studies of infrared absorption, though beyond the scope of this review, may be represented by citing the work of Hampton (302), Saunders & Smith (303), and Hart & Meyer (304) on rubbers, and that of King, Hainer & McMahon (305) on polymers at liquid helium temperatures. Infrared dichroism of polymers has been studied by Ambrose, Elliott & Temple (306, 307). The intensity and polarization of fluorescence in solutions of polystyrene has been measured by Heintz (308, 309). Brechbuhler & Magat (310) have measured the polarization of fluorescence in solutions of polystyrene containing strongly fluorescent catalyst fragments, of the order of one per molecule. From the calculated lifetime, it was concluded that approximately two monomer units participated in the rotary Brownian movement of the fluorescent group.

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## ION EXCHANGE<sup>1</sup>

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An ion exchanger may be pictured as resulting from two normally incompatible components, a conducting electrolyte solution (A) and a cross-linked polymer (B), as shown diagrammatically in Figure 1. The properties of component A are determined by the nature and the concentration of the electrolyte and by the nature of the solvent. The solution conducts current by movement of ions of both signs; concentration can be varied freely, between the saturation value and any infinitesimally low value, by simple dilution with solvent. The properties of the polymer B depend upon the nature of its bifunctional monomer, its polyfunctional monomer, and the ratio of the two which determines the degree of cross-linking. The cross-linked resins are insoluble in water and most solvents and are electric insulators.

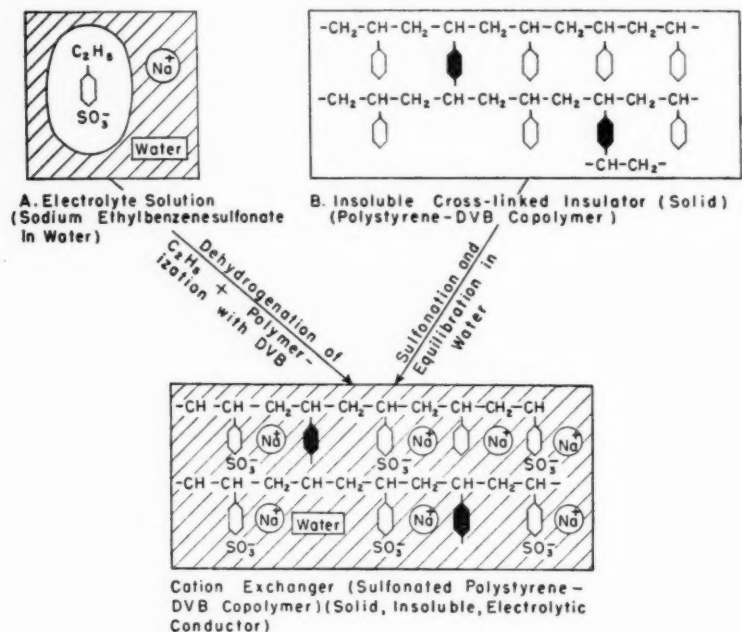
Chemical modification of either component can result in the formation of an ion exchanger. A is illustrated in Figure 1 by the sodium salt of ethylbenzenesulfonic acid dissolved in water as the solvent, B by a cross-linked polymer of styrene and divinylbenzene. Thus, the cation exchanger of Figure 1 can be pictured as resulting from A (by hypothetical dehydrogenation of the ethyl group followed by polymerization in the presence of divinylbenzene), or as resulting from B (by sulfonation followed by equilibration in water). Upon the formation of the exchanger some characteristics of each component are lost. The exchanger is no longer a solution, nor subject to infinite dilution with solvent, as A was, and it is no longer an insulator, as B was. Upon leaching and equilibration with solvent, it is a solid insoluble polymeric gel swelled (or "solvated") by the solvent which causes ionization of the functional groups into "fixed" ions linked to the polymeric matrix and "counterions" which are mobile in the gel solvent. A typical aqueous strongly acid (cation-exchange) or strongly basic (anion-exchange) gel will be composed of about 45 per cent of organic polymer, 45 per cent of water, and 10 per cent of functional groups, all by weight.

All properties and uses of ion-exchange materials can be related to this picture. The combination of the two components leads to a series of properties characterizing the ion-exchange phase (see Figure 1): (a) The electrolytic component has been linked to a polymer as a functional group which determines the character (anion exchanger, cation exchanger), the selectivity and the electrolytic "strength" of the exchanger phase (sulfonics, quaternary amines are "strong," carboxylics and tertiary or secondary amines are "weak"). Upon ionization of the functional group, one kind of ions becomes

<sup>1</sup> The survey of literature pertaining to this review was concluded in February, 1953. The survey of January 1953 is necessarily incomplete.

<sup>2</sup> The authors wish to acknowledge the efforts of M. E. W. Torok in compiling the literature references.

mobile in the gel solvent, whereas the other remains a fixed part of the polymer, that is, it does not move under a concentration or an electrical gradient. This characteristic forms the basis not only of ion exchange, but also of the



#### Characteristics of an Ion Exchanger

##### Nature of a Functional Group

- (a) Character of Exchanger including selectivity  
(b) Electrolytic Strength

##### Fixed Ion Effects

- (a) Ion exchange  
(b) Ion exclusion  
(c) Selective ion transfer (transport number)  
(d) Minimum conductance  
(e) Endosmotic water transfer

##### Capacity and Solvent Content

Column operational characteristics.

Steric factor due to cross-linked polymer

Ionic and molecular size-diffusivity into gel.

FIG. 1. Diagrammatic description of an ion exchanger.

newer fields of ion exclusion and of selective electrochemical ion transfer; (b) concentration has become "capacity" (as milliequivalents of functional groups per unit volume or weight, for example); (c) the solvent content of the leached wet gel has become fixed, its value being determined for each

solvent and counterion species by the electrolytic character of the functional groups, the ratio of functional groups to organics, and the nature and degree of cross-linking; (d) the cross-linked polymer has introduced a steric factor decreasing the accessibility of the gel phase to ions and molecules as their size increases.

A review concerned with the rapid development, during the ten year period from 1940 to 1950, of the field of ion exchange, based on well-defined, synthetic organic polymers, was presented by Boyd (15) in 1951. Boyd stressed the synthesis of exchangers, their chemical structure, the physical chemistry of exchange systems including equilibria and kinetics, the development of ion-exchange chromatography, the application of ion exchange to separation, and, more briefly, to analytical and preparative chemistry. In 1952, Bauman, Anderson & Wheaton (6) summarized advances along these lines made in 1951 and extended their review to include a detailed discussion of the characterization of exchangers, their use in organic catalysis, their screening effect as a function of ionic size, molecular adsorption by ion exchangers, and advances in the fields of ion-exchange membranes and polyelectrolytes.<sup>3</sup>

In 1952, ion exclusion (59) was announced as a new tool utilizing exchangers to separate ionic from nonionic solutes. Ion exclusion relies on the preferential diffusion of small nonionic molecules into the exchanger phase. It has been extended to separations of nonionic solutes of different diffusivity.

Interest in nonaqueous ion-exchange systems has grown considerably during the past year, with most efforts directed to the study of the equilibrium distribution of ions and solvents between exchanger and solution and to the removal of ionic constituents from nonaqueous solvents. Electrochemical studies on alcohol-solvated membranes have also been initiated.

The development of ion-exchange membranes and their use as hydraulic separators of electrolyte solutions has led to the study of selective ion transfer across membranes in electrolytic cells (6, 60), with particular emphasis on demineralization of water. This new interest is based on the observation that ion-exchange membranes rely, in the limit, solely on ions of like sign to carry electrolytic current in the membrane phase while maintaining the high specific conductance characteristic of relatively concentrated solutions; owing to the fixed capacity, any given "solvated" leached membrane has a finite minimum specific conductance. Further, the fixed charge is responsible for any endosmotic water transport accompanying electrolytic ion transfer.

Accordingly, in addition to a survey of last year's advances in (a) physical chemistry of the ion-exchange process and (b) applications of "conventional" granular materials, continuing the previous reviews by Boyd and by Bauman, Anderson & Wheaton, the present article will emphasize topics which have recently tended to broaden the field, namely, (c) ion exclusion, (d) ion exchange with nonaqueous solvents, and (e) electrochemistry of ion-

<sup>3</sup> Although the field of linear polyelectrolytes is closely related (ion exchangers are cross-linked polyelectrolytes), space limitations make it necessary to omit a discussion of this relation.

exchange membranes, including some applications (demineralization of aqueous solutions, separation of ions of like sign, and electrolytic preparations).

As to other uses of ion exchangers which are considered outside the scope of this article, reference is made here to recent reviews by Kressman and by Kunin which cover, among other topics, ion exchange as a unit process (73, 75) and the use of exchangers in analytical chemistry (73, 74, 75), in organic chemistry (73, 75), and in the biochemical and medical fields (73, 75); finally, brief reference is also made to new types of ion-exchange materials, including phosphonic resins (16, 30, 31), "electron" exchangers (24, 83, 111, 138), and chelating resins (51, 69), and to a number of new techniques of column operation (35, 147) and of regeneration and exhaustion (62, 98, 131).

#### PHYSICAL CHEMISTRY OF THE ION-EXCHANGE PROCESS

Knowledge of the *equilibria* between granular ion exchangers and their solution environment has advanced considerably during the past year. Since Bauman & Eichhorn (7) and Juda & Carron (61) ascribed an ionic solution character to exchange resins, the chronic failure of the law of mass action to provide truly constant equilibrium "constants" has usually been attributed to the lack of knowledge of the activity coefficients in the resin phase. A review of the current theory with respect to this problem has been presented by Glueckauf (46), and two later papers, one by Glueckauf (47), the other by Duncan (37), deserve special attention.

Treatment of the ion exchanger as a concentrated aqueous electrolyte by Glueckauf (47) has provided a valid theoretical interpretation of ion-exchange equilibria which predicts reasonably accurate values of distribution constants from osmotic data obtained for various monovalent ions with cross-linked polystyrene sulfonates. With few exceptions the calculated equilibrium constants agree with both the absolute values and the trends observed experimentally for different cross-linking, ions and solution compositions. In this study the water uptake, at different vapor pressures, of the polystyrene sulfonates was studied for H, Li, Na, K, and Ag.

Calculations were also made for the osmotic properties of an unstrained (*i.e.*, low cross-linked) resinate; that is, osmotic coefficient curves were plotted for the cationic forms of an exchanger with only 0.5 per cent divinylbenzene cross-linking which apparently differs little from a polyelectrolyte solution or from a toluenesulfonate. A comparison of these curves with the corresponding curves for HCl, NaCl, NaNO<sub>3</sub>, and Li toluenesulfonate showed that the anions of the resinate did not contribute toward the statistical entropy terms of the solution, but that otherwise the osmotic coefficients of the monovalent cations of the resinate were similar to those of strong 1:1 electrolytes.

Regardless of the present inadequate status of the theory of concentrated electrolytes, this approach should be tested, using further the numerous data already obtained on the swelling, water content, exchange capacity, and



equilibrium water vapor pressure of the various types of ion exchangers as a function of ionic strength, ionic form of the resin, degree of ionization, and percentage cross-linkage of the resin-polymer structure.

The review by Bauman, Anderson & Wheaton (6) provides a rather complete compilation of such data reported through 1951. In addition, the osmotic measurements presented in the Glueckauf paper for a strongly acidic exchanger are available for further study. The swelling and shrinkage of sulfonated polystyrene resins of different cross-linking have been measured by Pepper, Reichenberg & Hale (102). Gregor, Sundheim, Held & Waxman (50) have reported water-vapor sorption studies on exchange resins. Swelling values on weakly basic resins have recently been reported by Davies & Jones (32).

To calculate activity coefficients in the resin phase, Duncan (37) also considers an ion exchanger as a concentrated aqueous polyelectrolyte. He assumes that a cation exchanger and a 1:1 electrolyte solution having a single common cation, constitute a mixture of two 1:1 electrolytes in which one (the resinate) has only one mobile ion per equivalent. On this basis he has derived an expression for the activity coefficient of the resinate in the mixture which is analogous to, but not identical with the Harned rule for ordinary 1:1 electrolytes, that is  $\alpha_{12}$  (Duncan) =  $\nu a_{12}$  (Harned & Owen) where  $\nu$  is the number of mobile ions formed from one molecule of electrolyte. This leads to a calculated absolute value of the activity coefficient of the H-resinate, using infinite dilution as the standard state.

An activity coefficient versus molality curve has been obtained for the H-resinate and extended to very high concentrations, by combining osmotic data reported in Glueckauf's paper (47) with the calculated value of the H-resinate activity coefficient; it appears that at high concentrations there is less ion-pair formation for resinates of the sulfonated polystyrene type than is observed in aqueous solutions of corresponding nitrates at the same ionic strength.

Bonner, Argersinger & Davidson (2, 13, 14), in an extensive study of the sodium-hydrogen and the silver-hydrogen exchange on a sulfonated cross-linked polystyrene resin, have calculated equilibrium constants and activity coefficients of the resinate by means of the Gibbs-Duhem equation. In support of the validity of this approach, they have shown that the values of both, calculated from experiments, are independent of the ionic strength of the external solution.

Wiklander (144) has attempted to explain ion-exchange behavior on the basis of the Donnan equilibrium. Gregor (49) has attributed failure of the mass-action law to ion-pair formation in the resinate. An empirical equation which postulates a lattice model and describes the variation of the mass-action equilibrium constant as a function of exchange percentage has been derived by Sakai and co-workers (107) and applied to equilibria of solutions with organic and inorganic exchangers (108).

Högfeldt (57) has obtained the silver-hydrogen exchange isotherm by

titrating the hydrogen-saturated resin with standardized silver nitrate solution, the equilibrium silver-ion concentration being determined by e.m.f. measurements. These isotherms agree with isotherms based on batch-equilibrium studies of the same system. According to Saunders & Srivastava (112) nicotine, pyridine, piperidine, ephedrine, and quinine equilibria on carboxylic exchangers do not obey the same relation, with the weaker bases approaching mass-action behavior, whereas the stronger deviate considerably. Peterson & Jeffers (103) found that strongly basic resins take up aliphatic acids from concentrated solutions in amounts exceeding their exchange capacities. Recently reported were studies of cation exchange in phosphonous and phosphonic resins by Bregman & Murata (16), in alginates by Mongar & Wassermann (92), and in clay minerals by Eriksson (38).

The mechanism of cation and anion exchange in aluminous clay minerals and polyamine resins, respectively, has been considered by Cook and co-workers (28). Their thermodynamic treatment resulted in a good correlation with experimental data as well as in an explanation of the effects of ionic strength. They consider the mechanism of the exchange process as an (acid-base) ion-pair adsorption process in which one ion of the ion-pair is adsorbed on the solid or colloidal particle in a "compact double layer" while the other remains hydrated and occupies a "diffuse double layer." A new theory of cation distribution in silicates presented by Ramberg (104) emphasizes the importance of the electronegativity values of the metal and oxygen atoms in the clay structure.

Experimental information on *steric effects* has been concerned with the screening of ions based on their size and on the pore size of the exchanger. Examination of resin pore size has recently been accomplished by Kressman (72) and Partridge (99) with the aid of large ionic species. Above a minimum ionic size the saturation capacity and rate of approach to saturation is an inverse function of ionic size in a given, highly ionized, cross-linked exchanger. For this reason the order of equilibrium uptake of organic bases, as compared to that of smaller ions such as  $\text{Na}^+$ , is different from that predicted from basicity considerations, namely,  $\text{N}(\text{CH}_3)_4^+$ ,  $\text{N}(\text{C}_2\text{H}_5)_4^+$ ,  $\text{Na}^+$ ,  $\text{C}_6\text{H}_5\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_5$  instead of  $\text{Na}^+$ ,  $\text{N}(\text{CH}_3)_4^+$ ,  $\text{N}(\text{C}_2\text{H}_5)_4^+$ , and  $\text{C}_6\text{H}_5\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_5$ . Anomalies observed in the high saturation capacities of larger ions such as  $\text{C}_6\text{H}_5\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_5$  and  $[\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_3]_2^{++}$  have been attributed either to some orientation of these molecules during passage along the resin pores or to considerable distortion of the resin structure because of large attractive forces. On weakly basic, highly porous resins the equilibrium distribution of a series of ions has been found to be independent of ionic size and to favor ions with increased valence.

Interest in *kinetic studies* has continued during the last year. Soldano & Boyd (122) have investigated self-diffusion in several different exchangers. The two rate-controlling mechanisms in ion-exchange reactions, namely solution film diffusion and solid (resin particle) diffusion, have been studied

by Grossman & Adamson (52) who have derived equations by which the relative contribution of each can be determined. Faucher, Southworth & Thomas (39) have reported a fundamental chromatographic study of a clay mineral, assuming solid diffusion as the rate-controlling factor. The kinetics of fixed-bed operation under solid-diffusion controlling conditions has been further developed by Rosen (105) in an excellent mathematical treatment. The effect of longitudinal diffusion in ion-exchange and chromatographic columns has been considered in a discussion of the mathematics of adsorption in such beds (78). Michaels (91) has presented a simplified treatment of fixed-bed kinetics applicable to high exchange rates. This treatment is based on the concept of an exchange zone which descends through the bed at constant velocity. A quantitative calculation for interpreting and predicting the ion-exchange chromatography of trace components in fixed-bed separation columns has been developed by Vermeulen & Hiester (139). The saturation performance of exchange and adsorption columns has been analyzed by these same investigators (54) to explain and calculate regenerative operations in mixed beds.

An interesting new approach to *characterization* of ion exchangers has been used by Waldo & Frizzell (141); they employed infrared analysis to identify functional groups (sulfonic groups, OH groups, C=C bonds, and groups in *para* position) for several sulfonic resins. Capacity measurements and the identification of functional groups in various cation exchangers by the standard pH titration method have also been reported (120). Data for the standardization of methods employed in the rapid evaluation of ion exchangers on the basis of their exchange rates have recently been compiled by Zimmermann (149).

#### APPLICATION OF GRANULAR ION EXCHANGERS

The role of ion exchangers in *catalysis* has been reviewed last year by Bauman, Anderson & Wheaton (6) with emphasis on the catalytic hydrolysis of various esters by strongly acidic cation-exchange resins. A lengthy dissertation describing the performance of a continuous tower reactor (109) for such reactions supplements the earlier summary by Bauman *et al.* On the basis of batch hydrolysis of esters in aqueous solution. Davies & Thomas (33) have concluded that the catalytic process is essentially surface-controlled and that the resins are more effective catalysts, on an equivalent basis, than hydrochloric acid (increasingly so as the molecular weight of the ester increases). These results disagree with those obtained by Haskell & Hammett (53), probably because Haskell & Hammett used 70 per cent acetone rather than water as the solvent. Studies of the decomposition of diazoacetic ester and of nitrosoalkylurea in the presence of ion exchangers containing quaternary ammonium groups have been reported by Lautsch & Rothkegel (79). Selectivity in the hydrolysis of esters or ethers as a function of the size of the reacting molecules has been demonstrated in a study with a

strongly acidic and a strongly basic exchanger (34). Little catalytic effect of the resin on the hydrolysis of high-molecular-weight compounds was observed.

Some catalytic properties of montmorillonite have been investigated within the last year (66). Its effect is marked, for example, in the inversion of sugar, in the formation of sulfanilic acid from sulfuric acid and aniline, and in the formation of an anionic colorant containing helianthine from sodium nitrite and methylaniline.

Schmidle & Mansfield (117) have described a wide variety of reactions including cyanohydrin formation, benzoin condensation, diacetone alcohol formation, cyanoethylation, and nitro alcohol formation, which are based on anion-exchange catalysis. Anion exchangers are effective in the aldol condensation (5), the Knoevenagel condensation (4), the cyanoethylation of alcohols (3), and the preparation of 1,2,4-trichlorobenzene from a mixture of the  $\alpha$ - and  $\beta$ -isomers of benzene hexachloride (43).

Cation exchangers have been used as catalysts in polymerizations (29), in the inversion of sucrose (58), and in the splitting of cumene hydroperoxide to phenol and acetone, the last step of a preparation of phenol from benzene and propylene (26).

Ion exchange has been used as a tool in the *study of electrolyte solutions* (6), particularly for the determination of the relative activities of trace ions in mixed electrolyte solutions of different ionic strength. By such a technique Betts & MacKenzie (8) have obtained activity coefficients of the chlorides of sodium, potassium, rubidium, and cesium at effectively zero concentration in hydrochloric acid solutions varying in concentration from 0.005 to 1.5 *M* and activity coefficients of sodium chloride in solutions of lithium and potassium chloride. Measurement of the formation constants for the complex ions formed between calcium and strontium and a series of mono-, di-, and tricarboxylic acids, accomplished by a similar tracer technique, has been reported by Schubert (118, 119).

Application of the mass-action expression to ion-exchange equilibria with mixed electrolyte solutions has been made by Strickland (133) in order to determine the charge of ions in complex electrolyte mixtures. Similarly, Salmon (110) has reported the identification of a phosphate complex of trivalent iron in the presence of orthophosphoric acid.

The positive character of the halogens when prepared as nitrates in absolute alcohol has been established by the exchange of iodine and bromine with the hydrogen of a cation exchanger (17, 18, 67).

Interesting new developments in *separation techniques* involving complexing have become possible by ion exchange. [See Boyd (15), Bauman (6), and Tiselius (137); for recent separations of this nature refer to (20, 41, 93, 100, 128).] Advantage has also been taken of the differences in rates of exchange of ions of varying size to provide another separation technique. Thus, Kressman (72) has been able to separate inorganic acids from large dye acids as well as organic dye acids of differing size.

## ION EXCLUSION

Wheaton & Bauman (142) have made a significant contribution to the field of separation of nonionic from ionic compounds in solution. In ion exclusion the separation is due to the different distribution of the two solutes between solvated exchanger and the solution in equilibrium with the exchanger. Referring to Figure 1, the fixed capacity of an exchanger causes an equilibrium condition which, omitting activity corrections, may be apportioned in terms of concentrations ( $r$  denoting the resin and  $w$  the water phase).

$$(A^+)_r(B^-)_r = (A^+)_w(B^-)_w \quad 1.$$

Since the total concentration of  $(A^+)_r$  in a cation exchanger, for example, includes the mobile counterions of the fixed ionized matrix, the concentration of electrolyte which has diffused into the exchanger phase is always lower than that in solution (the exclusion being the better the lower the solution concentration). Realizing that no such exclusion should occur for nonionic solutes, Wheaton & Bauman predicted an effective separation of the ionic from the nonionic solute upon percolating a feed solution of the two solutes and a pure solvent (water) alternately through an exchange column.

Calling  $V_1$  the interstitial (*i.e.*, void) volume of the column and  $V_2$  the volume of solvent (water) in the exchanger, a volume  $V_1$  of feed can be passed through the water-filled column in the ideal case of complete electrolyte exclusion before the ionic constituent breaks through, whereas the nonionic solute will appear only after passing a volume equal to  $V_1$  plus  $V_2$  (assuming ideally equal concentration of the nonionic solute in the resin and in the solution). If this is followed by rinsing with water, a volume  $V_1$  will remove all the electrolyte left in the column, whereas the removal of the nonionic solute requires  $V_1$  plus  $V_2$ . In practice, exclusion never being ideal, the feed volume is always considerably smaller than  $V_1$  and the rinse volume considerably larger than  $V_2$ . To illustrate, Wheaton & Bauman used a 100 ml. column of a sulfonated polystyrene-divinylbenzene copolymer, having  $V_1$  equal to about 30 ml. and  $V_2$  equal to about 42 ml., a feed mixture of hydrochloric acid and acetic acid in water of about 15 ml., and they eluted with 100 ml. of water. Figure 2 shows the elution pattern with complete separation, acetic acid being practically nonionized in the presence of hydrochloric acid. A cyclic operation is of course possible.

This principle can be extended to separate solutes of different ionization constants,  $K$ . Wheaton & Bauman state the following requirements for successful operation of ion exclusion:

$$\begin{aligned} \text{Ionic fraction: } K &> 5 \times 10^{-2} \text{ Required} \\ &> 2 \times 10^{-1} \text{ Preferred} \\ \text{Nonionic fraction: } K &< 2 \times 10^{-1} \text{ Required} \\ &< 5 \times 10^{-2} \text{ Preferred} \end{aligned}$$

Because of the decreased electrolyte exclusion, separations become more

difficult as the electrolyte concentration increases in the solution, whereas the nonionic concentration is not subject to the same limitation.

A wide choice of resins is available for the operation of ion exclusion. In general, high capacity and high degree of cross-linking favor ion exclusion, but slow the diffusion and reduce  $V_2$ . Thus, a compromise between high and

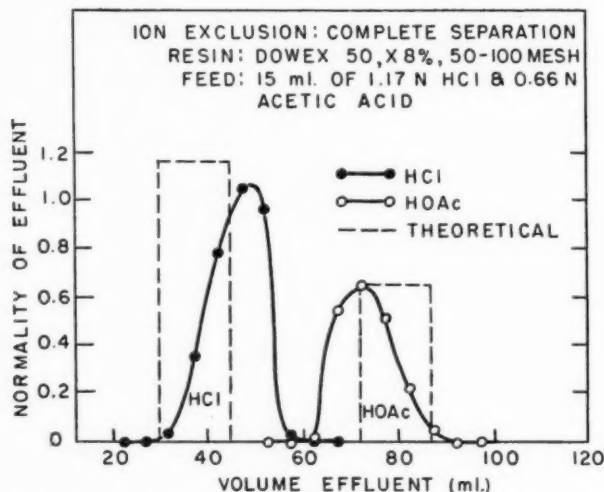


FIG. 2. Ion exclusion [Wheaton & Bauman (142)]. Reprinted by Permission of Dr. D. O. Myatt, Industrial and Engineering Chemistry.

low degree of cross-linking is indicated. Ion exclusion operates on diffusion gradients and therefore necessarily involves a dilution of each of the components. But it requires no chemicals and it promises, therefore, economical commercial applications whenever evaporation is either unnecessary or inexpensive relative to the cost of the separated compounds.

Wheaton & Bauman noted that larger molecules such as sucrose or D-glucose did not diffuse sufficiently into the exchanger phase to render separation from salt practical. This initial limitation suggested to them an extension of the principle to the separation of nonionic solutes from each other. In a second paper (143) Wheaton & Bauman determined distribution constants ( $K_D$ ) of various nonionic solutes between resin and solution and predicted separation factors and conditions of separation. Reasonable separation was obtained, for example, of a feed consisting of 5 per cent solutions of sucrose ( $K_D=0.23$ ), glycerol ( $K_D=0.47$ ), triethylene glycol ( $K_D=0.71$ ), and phenol ( $K_D=2.94$ ).

## NONAQUEOUS ION EXCHANGE

Since interest in nonaqueous ion-exchange has increased considerably during the past year, a brief discussion of recent work in this field is presented here, although it is based mainly on published abstracts of papers, with the full text not yet in print.

Gottlieb & Gregor (48) have performed swelling and solvent-distribution measurements on resins in various organic and inorganic ionic forms equilibrated with solvent mixtures which included methanol-water, ethanol-water, isopropanol-water, and dioxane-water as well as some pure nonpolar solvents. The extent of resin swelling increased with the more polar solvents; it can be correlated qualitatively with the activities of the solvents in solution and with the osmotic properties of the resin. Estimates were made of ion-pair formation expressed as a function of the dielectric constant expected for the gel phase.

Feinland & Gregor (40) studied the cation-exchange equilibria of various inorganic and organic cations in mixtures of methanol-water, ethanol-water, and acetone-water with sulfonated polystyrene resins of varying exchange capacity. The observed variation of distribution coefficients has been qualitatively explained on the basis of ion-pair formation as above.

Bodamer & Kunin (10) have also measured the swelling and the exchange of metallic and nonmetallic ions with ion-exchange resins in a variety of solvents. They conclude that swelling of a resin is not essential for the occurrence of ion exchange, many resins being porous enough to permit ready entry of ions without swelling.

Calmon & Wilich (21, 22) have suggested that swelling and deswelling of sulfonated low cross-linked polystyrene polymers (less than 1 per cent divinylbenzene) in mixed solutions of nonaqueous solvents and water can be used in the analysis of the solvents. For this purpose swelling curves have been plotted as a function of the equilibrium solvent-water composition of the solution phase. Solvents studied by these workers included methanol, ethanol, propanol, acetone, dioxane, and glycerol.

Measurements of electrochemical properties of ion exchangers equilibrated with nonaqueous solvents can also be expected to give a better insight into the dielectric properties of an ion exchanger. McRae & Lermond (80) have studied the conductivity of the hydrogen and lithium forms of a cation-exchange resin membrane of the phenolsulfonic acid type equilibrated with varying mixtures of methanol and water.

Chance, Boyd & Garber (25) have reported on the ion-exchange kinetics of sodium-hydrogen and bromide-hydroxyl exchange in various solvents. For this study two cation exchangers, one a weak acid and the other a strong acid, were used in column operation to remove NaOH from an 0.1 *M* solution in methanol, benzene, acetone, and ethylene glycol, singly or in binary combinations. Similarly, three anion exchangers, one a weak base and the two others strong bases, were used to remove HBr from an 0.05 *M*



solution in methanol, tertiary butanol, ethylene glycol, ethyl acetate, dioxane, benzene, acetone, and carbon tetrachloride, singly or in binary mixtures. In all cases the resin was regenerated with an aqueous solution and retained most of its water during the exhaustion cycle. The results indicate that ion exchange takes place between water-wet resin and several nonaqueous solutions, sometimes almost as rapidly as with aqueous solutions.

Column performance in nonaqueous ion-exchange operation has been analyzed recently by Vermeulen & Huffman (140). In this study experimental break-through curves are used to measure typical rate coefficients and to verify effects predicted for variations in concentrations, bed dimensions, velocity of flow, and particle size. An ion-exchange process which employs an organic eluting agent for the recovery of gold from cyanide solutions has been reported recently (19).

#### ELECTROCHEMISTRY OF ION-EXCHANGE RESINS

Membrane potentials and ionic mass transfer have been studied extensively in electrolytic cells with two or more compartments using selectively permeable polar membranes. Materials of widely different nature, including tissues of animal or vegetable origin, geological formations, glass, clay, and cellulose-based synthetic sheets have been studied as polar membranes; many among them have excellent selectivity to ions of one sign over ions of the opposite sign even when contacted with relatively concentrated electrolyte solutions. However, all have a high specific electrical resistivity. Such resistant membranes of good selectivity are particularly suited for e.m.f. studies in concentration cells involving little mass transfer, but their high resistance in mechanically stable thicknesses severely limits their use in electro dialysis.

It has been frequently suggested that the selective properties of such polar membranes are due to the presence of fixed ionic groups, but quantitative correlation between the concentration of these groups and electrochemical behavior proved to be difficult to establish because of the low concentration and the weakly dissociated character of the groups in the resistant membranes.

The recent development of synthetic resinous ion-exchange membranes having high specific conductance and a high concentration of fixed ionic groups has not only stimulated investigation of the electrochemical properties of synthetic organic ion exchangers, but has also led to considerable interest in their commercial use as mass-transfer membranes in electrolysis and electro dialysis cells. Membranes based on high-capacity synthetic ion exchangers have also been studied recently as membrane electrodes in concentration cells.

*Electrochemical properties* of ion-exchange membranes include selective transport of both ions and solvent under current, and electrolytic conductivity. These properties result from the presence in an ion-exchange resin

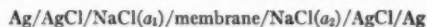
of mobile ions of a single sign, *i.e.*, either positive or negative. A conducting membrane has a capacity approaching that of commercial bead-type resins; this capacity corresponds to a concentration of mobile ions of a single sign comparable to a relatively concentrated aqueous electrolyte solution.

A second source of selectivity is the steric or "sieve" effect caused by the geometry of the polymer matrix which decreases or bars the diffusion of large ions into the membrane. This effect has often been related to an average pore size.

*Electrochemical membrane applications* employ (a) cells in which mass transfer across membranes is negligible, such as concentration cells and "bi-ionic cells" (of interest to biologists and physiologists and also to geologists studying oil-bearing formations); and (b) cells in which the mass transfer is significant, such as are used in electrolytic preparations and in electrodialysis designed to remove electrolytes from aqueous solutions and to separate ions of like sign.

*Electromotive force studies.*—There is a large body of literature on membrane potentials which arise when two solutions are hydraulically separated but electrolytically connected by a membrane having fixed ionic groups. The various membranes studied differ in origin, including animal tissues (42), vegetable tissues (145) geological formations (114), glass (36), clay (9, 94, 148), cellulose-based synthetic sheets (23, 44, 55, 56, 97, 124, 125, 148), and conducting and resistant resinous ion-exchange membranes (12, 27, 64, 82, 96, 101, 134). The common property of these diverse materials is that they show selective transport. The theory of the charged membrane potential, originally set forth by Meyer & Sievers (89; see also 87) and Teorell (135), has been recently expanded by several investigators (65, 68, 70, 95, 96, 113, 116, 132, 136). All of these studies deserve more space than can be devoted to them here, and a very much simplified picture is presented below.

The membrane potential may be derived from consideration of the cell



The e.m.f. of this cell is given by

$$E = 2RT/F \int_{a_1}^{a_2} t_{\text{Na}} d \ln a = (2RT/F) \bar{t}_{\text{Na}} \ln a_2/a_1 \quad 2.$$

where  $E$  = measured potential in volts;  $R$  = gas constant;  $T$  = absolute temperature;  $F$  = Faraday's constant;  $t_{\text{Na}}$  = transport number of  $\text{Na}^+$  in the membrane at equilibrium with solution at activity  $a$ ,  $a_1$ ,  $a_2$  = mean ionic activities of the two NaCl solutions at the two membrane faces, and  $\bar{t}_{\text{Na}}$  = average  $t_{\text{Na}}$  between  $a_1$  and  $a_2$ .

The membrane potential is equal to one-half of the above cell e.m.f., the other half being the electrode contribution. This equation holds for the condition in which no current is passed, *i.e.*, no mass transfer occurs, as prevails in the usual potentiometer circuit. If the transport number of a membrane is to be determined, it may be placed in a cell of this type with a solution of

known activity on each side, and the transport number calculated from the observed e.m.f.

In sufficiently dilute solutions, most selective membranes (resistant and conducting) are excellent membrane electrodes for univalent ions, acting as near-perfect cation- or anion-permeable membranes with  $t$  approaching unity. Generally, at solution concentrations approaching the fixed capacity of the membrane, diffusion of electrolyte (by Donnan absorption) into the gel structure lowers the transport number because *Fremdionen*, i.e., mobile ions of opposite sign to the mobile counter-ions normally present, become available to carry current, limiting the usefulness of membrane electrodes at these concentrations. Diffusion is always counteracted in part by the steric hindrance factor which tends to reduce the mobility of *Fremdionen*. The steric effect is particularly strong in membranes of specially modified colloid types reported by Sollner & Gregor (127). They are suitable as membrane electrodes for solution concentrations many-fold their capacities.

In 1949 and 1950, Wyllie & Patnode (146) reported the preparation of membrane electrodes of particularly good selectivity based on bonding dry exchange resins with insulating plastic binders, such as polystyrene. Of the presently known materials, these have given the highest membrane potentials in concentrated solutions (101). The most interesting case of excellent steric selectivity is that of the glass electrode used in pH measurements which limit passage of ions to hydrogen ions excluding sterically all others below a pH of about 12. At higher pH values, sodium ions begin to carry current, causing the "sodium error" in the common glass electrode.

If the transport number is known to be unity, and the ion activity on one side of the membrane is known, a potential measurement can be used to determine the ion activity on the second side under the following conditions: (a) If the transport is by a single ion, as in the glass pH electrode, where only  $H^+$  can carry current through the glass structure, the hydrogen-ion activity is determined; (b) If the same single electrolyte species is present on both sides, Equation 1 holds. This has provided an important use for various membranes in experimentation where the restrictions can be met, for example, in the study of activity coefficients in protein solutions (23) and in the study of shale beds in petroleum exploration (114).

Naturally, the question of determining individual ionic concentrations in mixed electrolytes arises. If a membrane separates a solution, say, of sodium chloride from a solution of potassium chloride at the same activity, a definite potential (called the bi-ionic potential, BIP) can be measured, and can be related to the relative strength of absorption and to the relative mobility of the two ions (86, 88, 123). However, if an unknown solution is placed on the second side of the membrane, containing undetermined quantities of potassium chloride and sodium chloride, the same potential measurement can be ascribed to an infinite number of KCl-NaCl mixtures (71, 82). A second measurement, say total potassium plus sodium, will be necessary to fix the

concentrations of the two species. If a third cation or a second anion is present, a third measurement must be made. Thus, in its present form a single membrane electrode will not determine a single ionic constituent in a mixture. (The notable exception to this is the glass electrode.) If membrane selectivity among cations were to be achieved similar to the selectivity of the glass electrode for  $H^+$  transfer, then the species to which it were selective

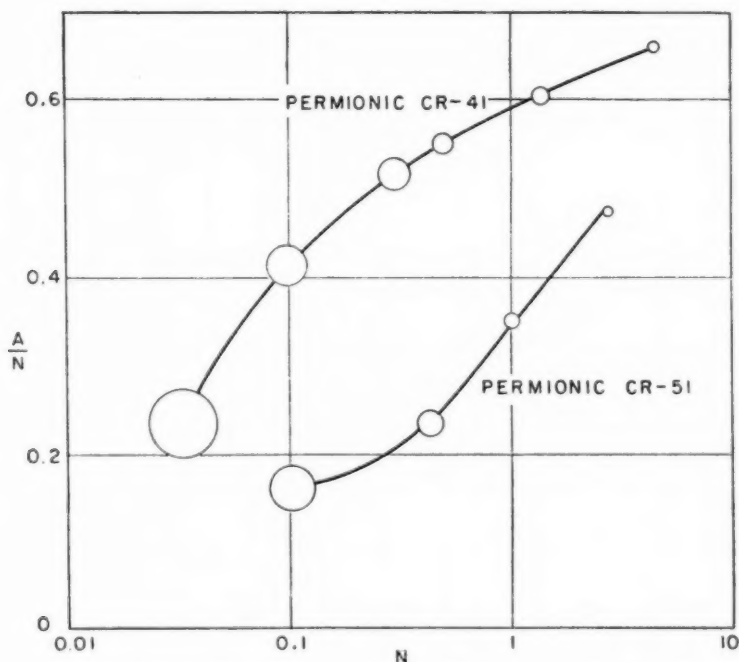


FIG. 3. Donnan diffusion of sodium chloride into Permionic membranes.<sup>4</sup>  
[Juda, Rosenberg, Marinsky, & Kasper (64).]

could be measured. Some of the newer selective resins (51, 69, 121) may, when formed into membranes, provide this useful analytic tool.

As predicted from the Meyer-Sievers and Teorell theory, the electrical resistivity (alternating-current measurement to prevent concentration polarization) approaches a constant value in dilute solution for those membranes

<sup>4</sup> These membranes which were first introduced under the trade name Permionic now are designated by the trade name Nepton.

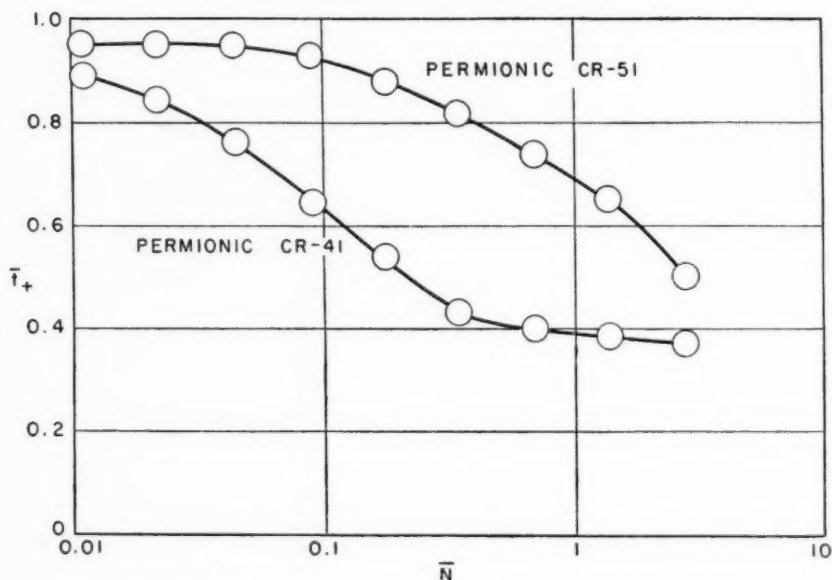


FIG. 4. Sodium transport numbers across Permionic membranes<sup>4</sup> in chloride solutions. [Juda, Rosenberg, Marinsky, & Kasper (64).]

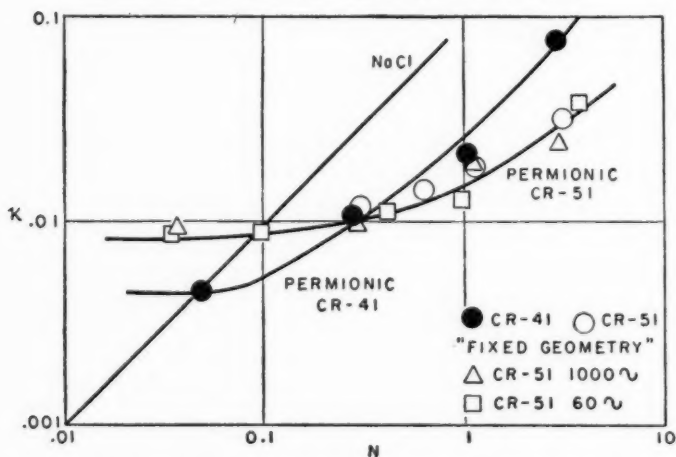


FIG. 5. Specific conductivity of Permionic membranes<sup>4</sup> CR-51 and CR-41 compared with specific conductivity of sodium chloride. [Juda, Rosenberg, Marinsky, & Kasper (64).]

on which resistance measurements have been reported (1, 27, 64, 84, 94, 115, 126, 127, 136). Leached conductances have been measured ranging from ion mobilities about one-fifth of aqueous values in homogeneous ion-exchange

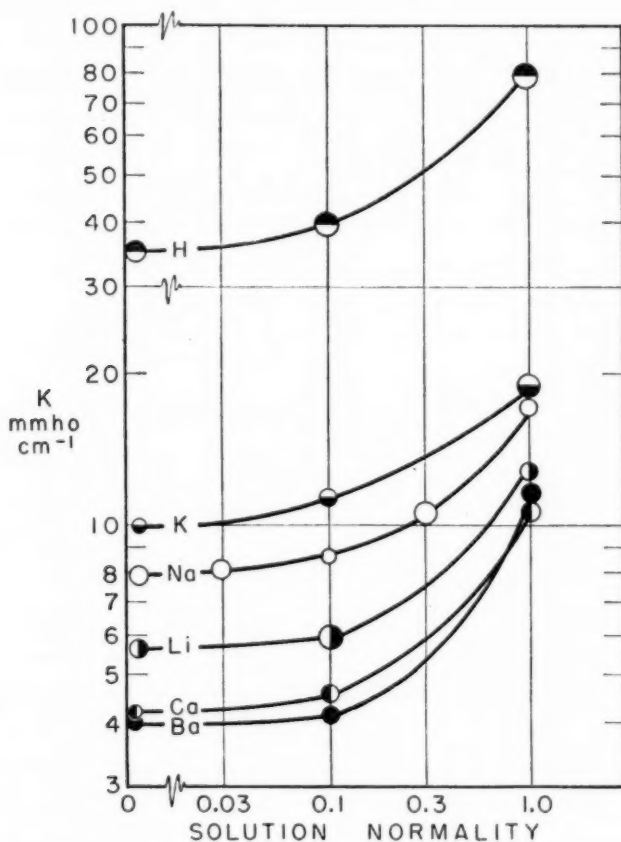


FIG. 6. Specific conductivity of various ionic forms of Nepton CR-51.

resins to the megohm resistances of the glass electrode, varying with the steric nature of the matrix, the degree of dissociation of the mobile ion, and the mobile ion capacity of the resin.

*Mass transfer studies.*—A battery of alternate cation-permeable and anion-permeable membranes separating alternating concentrated and dilute salt solutions has been suggested by Meyer (87) as a possible mechanism for the voltage generated by the electric eel. He constructed such a battery,

using membranes of treated cellulose, and found that high voltages could be obtained. The use of such a system to provide electrical power from mixing, say, of river water with the sea has been suggested (6).

Meyer (90) also operated this battery to create concentration differences between the alternating cells by imposing an electrical voltage across the ends of the system and measuring the cell potential at successive times, inferring therefrom the concentration gradients created. Manegold & Kalauch (85) and Billiter (9) studied the fundamental problems of mass transfer across charged membranes of porous clay and closely-woven cotton filter cloth or asbestos. However, the poor conductance, transport numbers, resistance to chemical attack, or mechanical properties of the membranes available at that time prevented practical usage of systems based on mass transfer through charged membranes under an applied voltage.

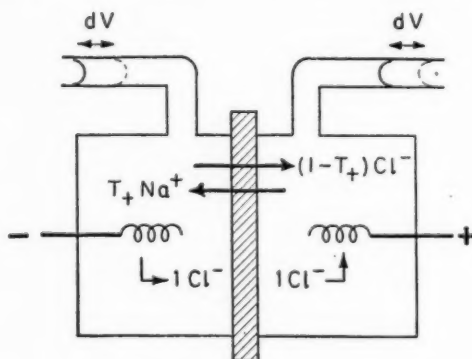


FIG. 7. Schematic drawing of transport cell.

In 1949, Juda & McRae (63) reported the preparation of conducting hydrated ion-exchange membranes. Since that time many ion-exchange resin-based conducting membranes have been studied (1, 12, 71, 76, 82, 96, 134). The dependence of transport numbers and conductance upon Donnan diffusion in any given solution environment is of importance to all electrolytic mass transfer cells. These properties have been correlated by Juda and co-workers (64), as shown in Figures 3, 4, and 5, for two cross-linked sodium polyphenol sulfonate membranes. The improved selectivity of one of them (CR-51) has been attributed to a lesser tendency toward ion-pair formation. Rosenberg (106) has investigated the conductance of this membrane in various ionic forms (Fig. 6) after equilibration with chloride solutions and has computed "dynamic" transport numbers from concentration differences resulting from current applied to the cell shown schematically in Figure 7. These values were in good agreement with transport numbers from e.m.f. measurements on the same membrane in sodium chloride. A considerable



transfer of water (ascribed to endosmosis) accompanied the salt transfer. These data are reported in Table I.

TABLE I  
DYNAMIC TRANSPORT NUMBER—STUDY OF THE CR-51- $\text{NaCl}$  SYSTEM

$N$	$V \frac{dN}{d \text{ meq}_{\text{el}}}$	$N \frac{dV}{d \text{ meq}_{\text{el}}}$	$T_+$	$t_{+e.m.f.}$
1	.54	.156	.70	.70
.3	.75	.083	.85	.83
.1	.92	.031	.95	.93
.03	.96	.009	.97	.95

$$T_+ = \frac{d \text{ meq}_{\text{Na}}}{d \text{ meq}_{\text{el}}} = \frac{d(NV)}{d \text{ meq}_{\text{el}}} = V \frac{dN}{d \text{ meq}_{\text{el}}} + N \frac{dV}{d \text{ meq}_{\text{el}}}$$

where  $N$ =normality of  $\text{NaCl}$  in the external solution,  $V$ =volume of solution in the cell,  $\text{meq}_{\text{el}}$ =milliamps./sec./96,500,  $T_+$ =dynamic transport number, and  $t_{+e.m.f.}$ =transport number from e.m.f. measurements.

An application of the cell of Figure 7 may be illustrated by the preparation of chloride-free caustic; at least in dilute solutions (with, e.g., salt as anolyte, graphite as anode, caustic as catholyte and iron as cathode) the cation-exchange membrane bars the diffusion of chloride ion into the caustic. Undoubtedly, many similar applications of such cells with both types of membranes (cation- or anion-exchange) will prove to be useful.

The demineralization of sea water at an energy consumption as low as 20 kw. hr. per 1000 gal. by means of conducting membranes has been reported (60) by the present reviewers and their associates. The nature of a demineralizer is such that the energy consumption per unit of water produced is proportional to the throughput per unit membrane area. Higher production rates can be achieved (lowering investment costs) by accepting higher energy costs, and vice versa. Furthermore, the useful life of the membranes (which are a major investment in such an installation) will determine the amortization rate, *i.e.*, volume throughput over which membranes must be expended.

Boer-Nieveld & Pauli (11) have presented data and an economic analysis of the desalting of water using ion-exchange membranes. They used both homogeneous ion-exchange resin membranes and cellulose-based membranes in their experimental program, and reported that high current efficiencies (*i.e.*, high transport numbers) were obtained in the transfer of salt in three-compartment cells, the center compartment being bounded by cation and anion membranes. They suggest that the use of a multimembrane system should be economically feasible on brackish waters. For example, they estimate 4 kw. hr. per 1000 gal. at a production of 1 gal./hr. ft.<sup>2</sup> for a demineralization of 1650 p.p.m. water to 500 p.p.m. based on data of the report. Brief

discussions of multi-membrane demineralizers, including diagrammatic drawings and analyses of some engineering problems were presented by Langelier (77) and Bauman, Anderson & Wheaton (6).

Another use of membranes as ion-transfer media is in the ionic fractionation still (45) shown in Figure 8. Such a still consists of a number of ion-

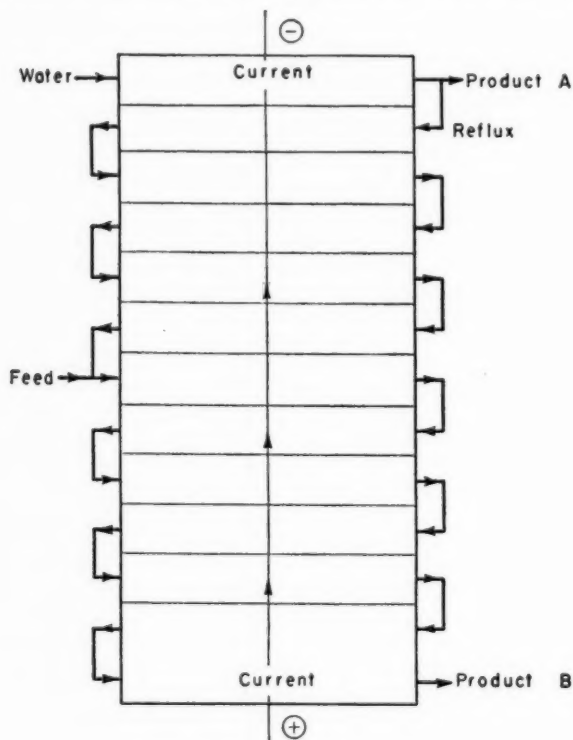


FIG. 8. Ionic fractionation still.

exchange membrane plates placed in an electric field and arranged at a small distance from each other, to permit repeated plate action. A flow of solution is maintained between the plates, and plate action is realized by transferring the ions electrically from the solution below each ion-exchange plate through the ion-exchange plate and into the solution above each plate. This enriched solution is allowed to flow downward (countercurrent to the electromigrating ionic stream) around the ion-exchange plates under conditions of partial reflux. An analogy drawn between the standard vapor fractionating still and

the ionic fractionating still by relating the heat source to the applied potential, the vapor to the electromigrating ions, and the countercurrent flow of liquid to the countercurrent flow of solution results in several equations which fully define the unit operation. The separation factors across membrane-solution interfaces and the variables affecting them, as well as the economics of this system, are under study.

The separation of ions in granular ion-exchange columns by ionophoresis has been described by Manecke (81); advantage is taken of the difference in migration rates of different ions in such a column. Still another type of mass-transfer study was carried out by Spiegler (129, 130), who attempted to regenerate an ion-exchange resin bed by electrolytic displacement of  $\text{Na}^+$  with  $\text{H}^+$ . He derived the transfer equations for this situation which were confirmed by experiments, indicating the current efficiency to be poor because the high mobility of the displacing  $\text{H}^+$  ion led to the creation of a diffuse boundary.

The versatility and usefulness of ion-exchange granules and membranes as theoretical and practical tools is receiving increasing recognition. Their application in many fields may be anticipated as materials of better electrochemical, mechanical, and chemical properties become available.

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# PHOTOSYNTHESIS<sup>1,2</sup>

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## INTRODUCTION

The large amount of recently published material in the field of photosynthesis precludes a general critical discussion in a short review of this kind. Emphasis will be placed on pigments, energy transfer mechanisms, and the Hill reaction rather than on quantum requirements and carbon dioxide fixation which were thoroughly reviewed in this series last year [Calvin *et al.* (1)]. We have taken the liberty of citing some material which was presented orally at the Gatlinburg Conference on Photosynthesis (October 29–November 1, 1952) in order to make the discussion reflect current research as much as possible. For more detailed information, and for other points of view, the reader is referred to the excellent reviews of Rabinowitch (2), Hill (3, 4), Whittingham (5), Franck (6), and French & Milner (7), together with the others mentioned in the text.

## PHOTOCHEMISTRY OF THE PIGMENTS

Despite the fact that the application of quantum-mechanical theory to large multiply-conjugated molecules like chlorophyll is in its preliminary stages, theoretical calculations of considerable promise have been made using combinations of the free electron and molecular-orbital methods. Chlorophyll and carotene energies and polarizabilities, together with their dependence on substituent effects, have received attention. The subject is soon to be reviewed by Platt (8) [see also Takeda & Oki (9)].

Recent experimental investigations on photosynthetic pigments have largely been concerned with chlorophyll. Livingston & Weil (10) now concur with Evstigneev *et al.* (11) in the belief that activators of fluorescence of chlorophyll exert their effect through the magnesium atom. There can be little doubt that this interpretation is correct since only metal tetrapyrroles show activation, and of these the magnesium chlorophylls alone show large effects, even when allomerized. Magnesium phthalocyanine, which lacks the pentanone ring, behaves like chlorophyll. Generalized bases of all types in nonpolar solvents or even slightly polar solvents without added bases raise the fluorescence yield of chlorophyll-*a* to approximately 25 per cent [Forster & Livingston (12)]. Fluorescence is essentially zero in dry hydrocarbons indicating loss to heat in less than  $10^{-12}$  sec. (13). The maximum fluorescence

<sup>1</sup> The literature survey for this review was completed in December, 1952.

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yield seems to be the same for all activating substances [Forster & Livingston (12, 14)] although some activators produce irreversible changes (14a). Livingston & Weil (10) measured the stability constants of chlorophyll-activator complexes and obtained values as high as  $1.6 \times 10^{-5} M^{-1}$ . This value is very large for interactions of magnesium via coordination and suggests that the metal atom maintains considerable electropositivity in the pigment. Magnesium has only a weak influence on the position of the spectral bands of chlorophyll-*a* (13) and hence plays a very similar role in the chemical properties of the first excited and ground states, perhaps a very small role since the presence of the metal only doubles the extinction coefficient in the red peak. Nevertheless, the latter fact supports the assumption of an electropositive magnesium atom, i.e., present as a magnesium ion held in place by electrostatic bonds, thus contributing part of its electrons to the chromophoric ring system.

Activators cause only slight changes in the extinction coefficients of the pigments relative to the large increases in fluorescence (13), indicating that these increases in fluorescence are not brought about by an increase in oscillator strength. Electronic excitation energy of one state can be lost externally to another molecule, internally in internal conversion to another electronic state (which may be stable or provide a pathway back to the ground state with the production of heat) or in fluorescence. Activator molecules therefore must increase the lifetime of the excited state by blocking some conversion process.

All activators influence absorption probability, spectral position and maximum fluorescence in the same way. This suggests that the activator has little influence on the electronic structure of chlorophyll, at least on the chromophoric ring structure. Activators would then be supposed to function simply by shielding the magnesium atom of the chlorophyll, most probably from other chlorophyll molecules to prevent self-quenching. Dimers or higher polymers of chlorophyll molecules of considerable stability would have to exist before illumination, since even weak activator-chlorophyll interactions destroy the polymer. Livingston and co-workers (private communication) have not, however, been able to find the competitive effects which would be expected between activators and chlorophyll for other chlorophyll molecules. We are therefore forced to consider the alternative explanation suggested by Livingston that activators, while apparently making little change in the electronic structure of chlorophyll, actually do alter internal conversion processes from the first excited singlet state replacing a state from which very rapid internal conversion is possible by the very different state. A verification and explanation for the latter puzzling phenomenon is obviously very important not only for understanding photosynthesis but generally for clarifying the reactions of the metallo-tetrapyrroles.

It is very probable that unexcited chlorophyll molecules do not dimerize to any considerable extent since spectral changes do not occur even at the very high concentrations where self-quenching is essentially complete

[(Rabinowitch (13); Aronoff (15))]. In view of the high polarizability of the molecule in its plane this fact is surprising. Perhaps the lack of interaction is due to the repulsion between magnesium atoms. The lack of spectral shifts in the presence of activators is also surprising since activators undoubtedly influence magnesium strongly and the latter atom in turn appears to have a large effect on at least one excited state. The problem is further complicated by the fact that no spectral changes occur in the presence of strong fluorescence inhibitors. Perhaps these quenchers lower the energy of the metastable state without influencing in any way the singlet states.

Whatever the role of activating molecules, the effect is to increase the lifetime of the first excited state from something less than  $10^{-12}$  sec. to about  $2.7 \times 10^{-8}$  sec. [25 per cent fluorescence yield (12), fluorescence lifetime of  $8 \times 10^{-8}$  sec. (13)]. Evidence based on the lack of change in chlorophyll fluorescence yield during its photosensitizing reactions strongly supports the view that these reactions occur from an excited state (probably a metastable triplet) reached by internal conversion from the original excited singlet state [reviewed in (13)]. Thus,  $2.7 \times 10^{-8}$  sec. would be the time for internal conversion to this state in the absence of quenching agents. However, it must also be remembered that spectral changes would be absent if the metastable state possesses a spectrum similar to that of the ground state. Before proceeding to new evidence pertinent to the metastable state, we shall consider what is apparently a quite different state produced in the photoreduction of chlorophyll.

In basic solvents like pyridine, photoexcited chlorophyll can be reduced by ascorbate, hydrogen sulfide, phenylhydrazine, dioxymaleate and cysteine in a process which has been extensively studied by the Krasnovskii group [(16, 17, 18); discussed in more detail by Rabinowitch (2)]. This type of reaction is slow and produces large spectral changes. It is almost completely reversible in strongly basic organic solvents. The reduced material returns to its original form by reaction with oxidizing substances. Compounds effective in the latter process include strong oxidants such as oxygen and the very weak oxidants DPN, riboflavin, and safranin. The latter substances can be reduced only at the expense of light energy. Confirmation of these results is necessary in view of their importance but is a reasonable expectation since the reduced form of chlorophyll is highly unstable with respect to the original pigment. As might be expected the ability to undergo photoreduction parallels fluorescence intensity for chlorophyll preparations, even when they consist of detergent-dispersed chloroplast fragments (19). Bacteriochlorophyll and bacteriopheophytin are reduced under similar conditions [Krasnovskii & Voinovskaya (20)] but since the latter substance lacks a metal atom, its reduction may be a different process. Alternatively this could indicate that reduction does not proceed at the magnesium atom.

Reducing agents generally fail to quench chlorophyll fluorescence but oxidizing agents including oxygen and quinone are quenchers in activating solvents [Livingston *et al.* (21)]. At least in the absence of reducing agents,

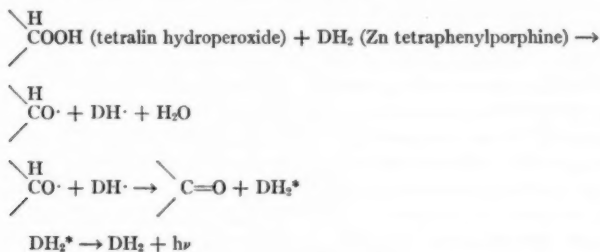
it must be concluded that the presence of an oxidizing agent favors the internal conversion process or introduces a new external process. Considerable study has therefore been made of the reactions of chlorophyll and oxidizing agents. The more recent studies have been particularly informative. Krasnovskii (22) studied reversible and irreversible photooxidations of activated chlorophyll, as have Linschitz and co-workers (23, 24); [also see Kachan & Dain (25)]. Both the latter teams found a bleaching reaction upon illumination at low temperatures in glassy solvents which could be attributed to a reversible oxidation. The Krasnovskii group studied a room-temperature reaction which is probably the same one, except that the temperature conditions favor rapid disappearance of the unstable oxidized form of the pigment. Bacteriochlorophyll and bacteriopheophytin are photooxidized in the presence of oxygen with the production in the former case of a peroxide-like compound with a spectrum resembling a porphyrin (20). These reactions are very poorly reversible at room temperature, probably as a result of subsequent reactions of the oxidized form. Photooxidation-reduction reactions of the iron analogue of chlorophyll are reversible and depend on whole-molecule light absorption [Ashkinazi & Dain (26)] even though the reactions occur at the iron atom. This suggests the use of light activation or inactivation as a means for studying the reactions of peroxidase and other heme-containing enzymes. Carbonylhemoglobin is known to undergo dissociation on illumination at the expense of the light energy [Bücher & Kaspers (27)].

Oxygen weakly activates the fluorescence of chlorophyll or magnesium phthalocyanine adsorbed on magnesium oxide, but cannot readily displace stronger activators such as ethanol vapor [Gachkovskii (28)]. Ethanol vapor alone shifts the fluorescence peak to 673  $\mu$ , and with oxygen added, the shift proceeds to 684  $\mu$ . This was regarded as a result of some reaction between the two types of molecules and was interpreted to mean that oxygen displaced ethanol on chlorophyll after which it removed hydrogen atoms from ethanol. A similar behavior is observed with water in place of ethanol. In both cases the information available does not indicate the precise effect of light. Potentiometric studies with metal electrodes upon which had been deposited layers of chlorophyll or related materials, while somewhat ambiguous, appear to support the adsorption studies just mentioned [Evstigneev & Terenin (29)]. According to Schenck (30) who worked with methanol extracts of leaves, illuminated chlorophyll forms an oxygen addition compound which is able to react with pinene by transferring the oxygen to form a 1 to 4 bridge across the phenyl nucleus. A number of other dyes in addition to chlorophyll are said to carry out similar reactions.

Linschitz *et al.* (23, 24), working at low temperatures, have been better able to follow the course of the reversible photooxidation of chlorophyll and their work tends to support the studies thus far discussed. In glassy solvent matrices on strong illumination the chlorophyll is bleached while added oxidants or even polar solvents are simultaneously reduced to the

extent of one electron. Similar results were obtained by Kachen & Dain (25). The reduced electron acceptor is then thought to attach itself to the radical form of the chlorophyll, perhaps at the magnesium atom since magnesium-free substances react only poorly (24). Allomerized chlorophyll does not react which suggests that the pentanone ring (ring V) participates in the reaction. One can speculate that this ring provides the electron or hydrogen atom transferred. If chlorophyll does react at the magnesium atom, a magnesium-nitrogen bond would have to break. In this case the excited pigment would behave as a Grignard reagent, a possibility which has been frequently suggested. It is interesting to note that under certain conditions, the first step of pheophytinization is accelerated by light and that once this has occurred, it can spontaneously reverse (31).

Chlorophyll, metal porphyrins and related compounds chemiluminesce at high temperatures [Rothemund (32)]. Recent studies have led to a suggested mechanism for this process which supports that proposed for low-temperature photooxidation [Linschitz (24)]:



This mechanism could contain all the required forms to serve, in its reverse direction, as a prototype light mechanism for photosynthesis. Indeed, radical intermediates of some sort have tentatively been identified by Uri in chloroplast fragments using the initiation of vinyl polymerization as an indicator (33). However the reversible photoreduction and oxidation reactions of chlorophyll and the chemiluminescent reactions all go with difficulty and all produce unstable intermediates with altered spectra. No such intermediates have been thus far detected *in vitro* or *in vivo* and none of these reactions appear to be as efficient as photosynthesis [(23); Duysens (34, 35)]. On the other hand, complete photooxidation reactions catalyzed by chlorophyll in activating solvents proceed easily with high quantum yields (31). We therefore must expect that oxidation and reduction proceed so nearly simultaneously that the chlorophyll remains unchanged. Probably both oxidizing and reducing substances form weak preliminary association complexes with chlorophyll as would be required to explain the high quantum yields of the *in vitro* processes if the lifetime of the reactive excited state is short. In particular, reducing agents may take the position of activator molecules

at magnesium. The cooperating molecules appear to accelerate mutually their own reaction through chlorophyll, and for this reason the fluorescence yield of chlorophyll should take on values determined by the concentrations of both, and perhaps their relative preillumination affinity for chlorophyll. Thus, we tentatively distinguish the reactions of the three-partner unit of reducing agent-chlorophyll-oxidizing agent from those involving chlorophyll and a single partner. The suggestion of close cooperation in the former case is supported by the studies of Weigl & Livingston who established (a) that no hydrogen exchange took place between chlorophyll and heavy water in organic solvents (36), and (b) that no permanent hydrogen exchange occurred between chlorophyll and deuterated ascorbic acid when the latter reduced the dye butter yellow in a chlorophyll-photosensitized reaction (37). We can favor a popular idea in photosynthesis that the over-all oxidation-reduction reaction involves the production of a triplet chlorophyll which loses an electron to an oxidizing agent and then immediately regains one from the reducing reagent (13). The hydrogen balance is probably most rapidly achieved by a transfer between the oxidant and the reductant. It would be difficult to decide at this time whether or not intermediate bonds occur at the magnesium or at a closely associated nitrogen atom. However, the available evidence does suggest that one unpaired electron of the chlorophyll diradical can appear at the metal atom. The ability of the metal atoms of metal-porphyrin prosthetic groups to gain unpaired electrons from the remainder of the molecule is thought to be a partial explanation of the reactions of some heme proteins [George (38)].

New isomers of porphyrins and chlorophylls appearing at low temperatures have been detected by their spectral shifts in the work of Freed & Sancier (39, 40). Linschitz (24) and Kachan & Dain (25) observed similar spectral changes. Recent reviews on chlorophyll include those of Rabinowitch (2), Aronoff (41, 42) and Stoll & Wiedemann (43).

#### CHLOROPLAST STRUCTURE

Work in this field was recently reviewed [Granick (44); Weier & Stocking (45)]. Most of the subsequent papers are concerned with studies on the fine structure of the chloroplast by use of the electron microscope. Qualitative agreement exists concerning the interpretation of the electron micrographs, and these results agree generally with the earlier suggestion of Frey-Wyssling and others [reviewed by Rabinowitch (31); Granick (44)]. Differences which do exist may result from differences in techniques and species of plants used.

Chloroplasts of the higher plants contain somewhat cylindrical grana which show a lamellar structure [Thomas *et al.* (46); Steinmann (47, 48)]. The lamellae may be readily separated by ultrasonic treatment (46, 47, 48), and appear to have a thickness of 70 Å (47, 48). It has been suggested (2) that the grana are composed of discs of proteinoid material held together by intervening fatty layers. Pretreatment of chloroplasts with enzymes and fat



solvents indicated that both the chloroplasts and the individual grana are surrounded by protein-lipoid membranes with an outer lipid layer (46). This may be responsible for the wax-like properties of isolated chloroplast fragments and the selective staining of grana by lipophilic dyes. Different parts of the chloroplast stroma show a different electron scattering power (49).

On the other hand, chloroplasts of the green algae studied showed a lamellar, rather than a grana-containing structure. *Euglena* chloroplasts were composed of approximately 20 dense, parallel layers with an average thickness of 250 Å separated by interlamellar spaces of 300 to 500 Å [Wolken & Palade (50)]. Similar results were obtained with *Poteriochromonas*. Lamellae 70 Å in thickness were found in *Spirogyra* and *Mougeotia* chloroplasts (47). The structural similarity of chloroplasts and the retinal rods of animals was suggested (46, 47). This similarity appears again in the section on energy transfer processes.

It appears that the chloroplast pigments are confined to the grana, and perhaps to the dense lamellae. Even in simpler organisms the photosynthetic pigments appear to be confined to particulate structures rather than being dispersed. All of the chlorophyll and carotenoids of the blue-green algae *Synechococcus cedorum* are confined to particles approximately 2200 Å in diameter, roughly the size of the grana of higher plants [Calvin & Lynch (51)]. Similarly, the pigments of the photosynthetic bacteria *Rhodospirillum rubrum* were found to be in chromatophores 400 to 600 Å in diameter [Pardee *et al.* (52); Schachman *et al.* (53)].

It is difficult to determine the localization and distribution of enzymes, nucleic acids, and other compounds of metabolic importance in chloroplasts because of the difficulty in obtaining chloroplasts free from other cell fractions [McClendon (54)].

The "chlorophyll lipo-protein" of Takashima (55) has been crystallized in this laboratory from 30 species of plants, and has been shown to be contained in washed chloroplast fragments. The chlorophyll appears to be adsorbed on the surface of the crystals rather than bound chemically (56). The material is of considerable interest, however, in that it may be a crystalline lipo-protein. Use of large molecular weight solutes, such as the polyethylenglycols, permits retaining a more normal morphology in isolated chloroplasts and results in the obtaining of the Hill reaction with chloroplasts from red algae [McClendon & Blinks (57)]. Smith *et al.* (58) showed that the development of Hill reaction activity by chloroplasts from barely leaves paralleled the conversion of protochlorophyll to chlorophyll. Roux & Husson (59) studied the incorporation of radioactive carbon into the chloroplasts of corn plants grown in a nutrient solution containing radioactive glutamic acid. The protein phycoerythrin has been studied by physical and chemical means [Kransnovskii *et al.* (59a)]. It apparently functions primarily as a means for energy transfer.

## ENERGY TRANSFER MECHANISMS

*Transfer among pigments.*—Electronic quanta can be transferred from molecule to molecule by mutual coupling of dipole fields in a process known as "sensitized fluorescence" or "induced resonance." The collection of photons at the initial chemical reaction sites in vision probably proceeds by such a process, as may the photosensitization of photographic emulsions by dyes (60). Dutton *et al.* (61, 62) first obtained evidence that energy transfers of this type were involved in photosynthesis, and the process has since been much studied in this connection. Recent investigations of energy transfer, or relative photosynthetic efficiency of pigments in plants, include those by Tanada (63), Thomas (64), and French & Young (65). The most complete study is that of Duysens (35), who systematically measured energy transfer in purple bacteria, diatoms, and in green, brown, blue-green, and red algae. By making relative fluorescence measurements, he showed that electronic excitation energy is transferred by a "bucket brigade" of pigments from those absorbing toward the blue end of the spectrum to those absorbing at longer wave lengths until chlorophyll-*a* or the form of bacteriochlorophyll absorbing at  $890 \mu$  was reached. Useful internal conversion apparently occurs only at these latter pigments or at chlorophyll-*d* when present since these alone show fluorescence. Generally speaking, carotenoids are approximately 50 per cent efficient in energy transfer, although fucoxanthol (63), which fluoresces farther toward the red than the others, has much higher efficiency. Phycobilins, phycoerythrins and chlorophyll-*b* are nearly 100 per cent efficient in transfer and in causing photosynthesis. Migration proceeds in one direction as might be expected if the migration time is longer than vibrational periods ( $10^{-13}$  sec.). In each step toward the red the electronic quantum of the emitter is converted into a lower energy electronic quantum of the absorber together with vibrational quanta which are dissipated before the reverse transfer process can occur.

The red alga *Porphyridium cruentum* and the blue-green alga *Oscillatoria* contain quantities of nonfluorescing chlorophyll-*a* which cannot participate in photosynthesis (35), possibly because it can lose its energy noneffectively to traces of chlorophyll-*d*. Phycocyanin energy migrates only to the fluorescent chlorophyll-*a*, and in this way phycocyanin appears more efficient per molecule than chlorophyll-*a*. These facts and interpretations probably explain the finding of just such a phenomenon by Haxo & Blinks (66). Duysens (35) assumed that energy absorbed in the blue bands of chlorophyll-*a* and -*b* was as efficient in fluorescence and photosynthesis as that absorbed in the red. This assumption is well supported by the findings of Forster and Livingston in pigment studies *in vitro*.

There are two general theoretical approaches to the phenomenon of induced resonance [Bayliss (67)]. The theory of Fraenkel & Peierls [Seitz (68)] for "exciton" migration applies to crystals and ordered arrays of molecules taking into consideration the interactions among distant as well

as nearest neighbors. Exciton migration is a common occurrence in many crystals and probably in the photographic process, and is usually due to the overlap of short-range electric fields. However in a recent extension of the theory, Heller & Marcus (69) have predicted that dipole-dipole interactions can produce exciton migration. A theory dealing with disordered arrays of molecules is probably required for studies on energy transfer in solutions and in plants. The most modern theory of this type is that of Förster (70, 71). Duysens (35) has compared his observations with the predictions of the latter theory. The calculations are uncertain to the extent of the estimates of the fluorescence yields of the various pigments in the absence of migration processes. In particular this estimate may be incorrect for chlorophyll-*a* *in vivo* since (a) the internal conversion time is unknown, and (b) the internal absorption of chlorophyll is probably very high in view of the fact that many chlorophyll molecules must be completely shielded by neighbors (see next section). In the presence of migration Duysens estimates the fluorescence yield as one per cent, but it may be higher in the absence of migration. Comparison between theory and experiment is generally good.

*Factors influencing spectrum position.*—According to Förster the spectrum shifts toward the red when strong coupling exists but the theory of exciton migration can allow similar predictions with weak coupling (72). The slow time of migration (as shown by the existence of vibrational equilibrium between each jump) implies that coupling is weak. Therefore large spectral changes should not be observed. The theory of Förster consequently is the one to apply to *in vitro* transfer among chlorophyll-*a* and chlorophyll-*b* molecules [Duysens (35); Watson & Livingston (73)]. Chlorophyll in solution shows no spectral shifts even at 0.1 *M* concentration [Aronoff (15)]. On the other hand, Strain (74) has observed red shifts to as high as 710  $\mu$  in the red peak of microcrystalline chlorophyllide-*a* comparable to the 745  $\mu$  value of Jacobs & Holt (75). The latter authors observed similar shifts in pheophorbide-*a* and -*b* and bacteriochlorophyllide. All these observations are probably explained as exciton phenomena depending on an ordered lattice. Krasnovskii *et al.* (76) were able to prepare solid films of bacteriochlorophyll from solutions of a single species of molecule which showed the same three infrared absorption peaks which this substance shows *in vivo*. Jacobs & Holt (77) have noted very large red shifts in highly ordered lamellae of chlorophyll molecules precipitated in the presence of calcium ion. The shift is proportional to the size of the individual particles, reaching a maximum at a particle size equal to that of a wave length of light. The lamellae of chloroplasts appear to possess thin planes of high electron scattering power which might correspond to the specimens of the latter authors. However much larger *in vivo* shifts would be expected than those observed and it might be expected that the marked ability of chlorophyll for self-quenching would be preserved in plants, which it is not [Duysens

(35)]. Comparison of fluorescence and spectral changes for the two types of lamellae may establish that the spectral shifts observed in plants correspond to those in the artificial preparations and this explanation is perhaps the most attractive available at present. However, we cannot discount other possible explanations including (a) compound formation of the pigments with protein or lipid, (b) physical adsorption or weak interaction among associated plant materials (28, 31) and (c) preferential adsorption of the lower temperature isomer [Freed & Sancier (40)]. Mechanism (a) is probably disallowed by the fact that no pronounced relative changes in peak position occur. The phytol tail of chlorophyll probably serves to position the molecule through adsorption to plant material. However, even strong chemical bonds through this tail would not alter the spectrum significantly whereas most primary bonds to the tetrapyrrole structure would be expected to produce large qualitative spectral changes. Shifts in spectrum due to mechanism (b) would be difficult to understand. Activating molecules produce only slight spectral changes while oxidants have no effect at all. Whatever the mechanism actually in effect, it must account for the nearly uniform spectral shift, the absence of self-quenching and the fluorescence yield.

*Energy transfer in vivo.*—The technique of velocity determination during periodic illumination has been extended to the Hill reaction of *Chlorella* by Clendenning & Ehrmantraut (78) and by Ehrmantraut & Rabinowitch (79) to permit comparison with the values originally reported for *Chlorella* photosynthesis by Emerson & Arnold (80). The maximum yield following a "saturating" flash was found by Ehrmantraut & Rabinowitch on extrapolation to be the same as that for photosynthesis. However, the relation between light intensity and yield was quite different. The authors concluded from these and quantum yield measurements that photosynthesis and the Hill reaction were identical in their observable parts in intact *Chlorella* cells. The large differences in yield observed for dark times giving less than maximum yield could be interpreted as indicating a difference between the two reactions. However, it is probable that these differences represent artifacts due to the quinone used as oxidant (see next section). Tamiya (81) using a sector wheel rather than a discharge tube for obtaining intermittent illumination, disagreed with Emerson & Arnold (80), finding a much longer maximum dark time and a temperature-dependent maximum yield per flash. Tamiya's results have been criticized on the grounds that his conditions allowed operation of the "limiting (dark) enzyme" during the flash as well as permitting induction phenomena (79). Gilmour's (82) preliminary measurements on chloroplast fragments using high light intensities and long flash times confirm the long dark time of Tamiya on a system free of induction phenomena. However, at lower light intensities the dark-time versus yield relationships as described by Emerson & Arnold are approximately duplicated by both Tamiya and Gilmour.

Förster (70, 71) proposed that the entire problem of energy collection in photosynthesis was solved by induced resonance among chlorophyll

molecules so that about 2000 chlorophyll-*a* molecules would feed their energy to a single molecule of the enzyme limiting the dark reaction at which one molecule of oxygen would be produced ultimately in a single act. As Franck & Teller (83) point out, the lack of strong mutual coupling among chlorophyll-*a* molecules probably invalidates this simple solution because weak coupling implies long times per jump and hence few jumps. The collection problem must then be broken down into two parts by assuming quanta are collected by smaller aggregates of pigment molecules and, once converted to chemical energy, are again collected in packets of 3, 4, 6, 8, or 10, depending on one's quantum yield preference, for some later process leading to oxygen formation [Duysens (35)]. In this way as few as 200 chlorophyll-*a* molecules could act as a collecting unit. Franck & Livingston (72) criticize Förster's theory on the basis of their calculations using a small *in vivo* fluorescence yield (0.01 per cent), which would permit only a few migration processes before conversion. However this calculation in turn may be subject to review in the light of Duysen's new estimates for the *in vivo* fluorescence yield (1 per cent). The latter author in a rough calculation finds a collecting unit of 200 molecules just possible, and we believe this to be a minimum figure. Some very recent support for a unit of this size is provided by comparison of Hill-reaction velocities at high and low light intensity from approximately monodisperse preparations of chloroplasts of decreasing size [Thomas *et al.* (84)]. Under both high and low light conditions the reaction rate decreased with particle size below a critical size of particle containing about 100 chlorophyll molecules as would be expected with the collection unit envisioned by Duysens. In any event, there is still required a second collection system about which at the present time there appears to be no direct experimental evidence.

#### THE HILL REACTION

*Components of the Hill reaction.*—We do not possess a formal kinetic mechanism for the Hill reaction of even a single plant species. Indeed, it is not possible at present to decide just which, and how many, of the component steps of photosynthesis are involved in the Hill reaction. It can probably be assumed that at least part of the carbon dioxide fixing system including Franck's enzyme A is not necessary. Chlorophyll is almost certainly involved in the slowest step of the light reaction. Otherwise it would not be expected that the absorbed light would be used with the demonstrated high quantum efficiency (see quantum requirement subsection). It is generally assumed (although never unequivocally proved) that chlorophyll-*a* concentration does not enter explicitly in the dark reaction of photosynthesis [see discussion in Rabinowitch (13)]. Experimental proof to the contrary would probably be difficult to obtain since there generally seems to be a close relationship between the chlorophyll concentration and the concentrations of the other photosynthetic components.

The general failure to detect intermediate forms of chlorophyll during

photosynthesis suggests that any cycle of chemical reactions in which the pigment participates in order to convert excitation energy into chemical energy must be very fast. This would be expected if the process proceeds by a combination of the oxidation and reduction processes discussed in the section on "Photochemistry of Pigments." These rapid transitions are probably assisted by nearby acceptor molecules present in fixed concentration. Both electron donors and electron acceptors would be required. Perhaps a single molecule such as part of Franck's enzyme B could possess both properties. It is not known whether water participates at this point in conjunction with one of the acceptors, although such a possibility is attractive.

If the observations on chlorophyll *in vitro* apply to plant systems, the relative available concentrations of activators and oxidizing acceptors probably control the degree of fluorescence. This suggests that fluorescence could be altered directly by contact with chlorophyll, or indirectly through activators and acceptors (see next subsection).

In addition to chlorophyll-*a* and initial energy acceptors at least one other catalytic component or acceptor appears to be required in plants to explain with the others the existence of three general types of extrinsic effects, (a) those which reduce both light and dark reaction velocities equally, (b) those which depress only dark reactions, and (c) those which depress the light reaction (possibly through an effect on chlorophyll as will be described below). The loci of the first two effects may very well consist of several catalytic components for each type, but in the absence of inhibition only two of these appear to participate in the observable slow steps. Of these two, one, at least in part, is a protein since it demonstrates the ultraviolet sensitivity of proteins [Holt *et al.* (85); Vereschinskii & Kransnovskii (86)], and is thermally denatured at high temperatures (35° C. and above) with the typical high entropies and heats of activation for this process in proteins [Bishop (87)]. Both light and dark reactions are apparently affected by thermal denaturation and by ultraviolet inactivation.

The interesting chemiluminescence reactions studied by Strehler *et al.* (88, 89) will provide information about one of the acceptors, but at present it cannot be unequivocally decided which one provides the storehouse for the energy ultimately emitted by chlorophyll in the chloroplast as light. The chemiluminescence is long-lived and of low intensity, and conforms closely in relative intensity to the relative velocity of the Hill reaction occurring at the same time. It takes place in *Chlorella* and in spinach chloroplast fragments after illumination. Strehler *et al.* provide abundant evidence that intermediates of chlorophyll-*a* are not the source of energy, although the first acceptor molecule might be. In the physiological pH range the dependence of intensity on pH is just the inverse of that of the dark step of the Hill reaction which suggests that chemiluminescence and the forward progress of the Hill reaction to products are competitive processes. Carbon



dioxide decreases the intensity of chemiluminescence in *Chlorella* indicating that one of the intermediates in carbon dioxide fixation reduction reacts at or beyond the high energy substance.

It is unlikely that oxidation and reduction processes, at least in the Hill reaction, are separated by many intervening steps. Mehler (90) and Gilmour (82) attempted to find a permanent storage of reducing power following illumination as would be required if the transient stages at the beginning of illumination were not completely reversible. The latter condition could not exist if some oxygen had been lost. Mehler's results were negative but inconclusive. Gilmour, in more extensive studies, corrected for the slow dark reduction of groups on the chloroplasts which can be detected in the absence of other oxidants (see next subsection). He was able to show that less than one molecule of light-produced reducing agent remained per 2000 chlorophyll molecules after a mixing process with titrating oxidant which was complete within one second following a single high intensity flash. With oxidant present before illumination, considerable permanent reduction occurred.

*Mechanism of the Hill reaction.*—A number of studies on the relation of the electron acceptor (oxidant) to the Hill reaction have appeared. Clendenning *et al.* (91) and others [Spikes (92); Ehrmantraut & Rabinowitch (79); Brin & Krasnovskii (93)] have shown that the rate of the reaction is dependent on the nature and on the initial concentration of the oxidant with both isolated chloroplasts and with intact *Chlorella* cells. This makes the interpretation of kinetic experiments difficult, since the specific effects of the oxidant employed must always be considered. Work on isolated chloroplast fragments (unpublished results, this laboratory) showed that especially anomalous effects occur with ferricyanide and with quinone over the range 0.002 *M*–0.04 *M*. Since the oxidant concentration changes during the course of an experiment, and since most manometric studies on the Hill reaction are carried out with oxidant concentrations in the above range, great care must be taken in interpreting most of the published results.

The possibility exists that oxidation and reduction processes may be more closely related in the Hill reaction than in photosynthesis in that the natural acceptor necessary for photosynthesis might be unnecessary. The artificial oxidants, most of all of which are strong oxidants compared with carbon dioxide, quench chlorophyll fluorescence in plants just as they do *in vitro*. Quinone, the only known Hill oxidant for *Chlorella*, not only irreversibly destroys photosynthesis in this organism by destroying or blocking the carbon-dioxide fixation system, but also reduces the chlorophyll fluorescence as it does in higher plants. Kautsky (94) quotes unpublished work of Zedlitz on the fluorescence of chloroplast fragments in which it was found that the Hill oxidants (oxygen, ferric oxalate ion and quinone) are quenching agents. Our studies on the Hill reaction show that quinone and ferricyanide behave similarly in that they inhibit the light reaction in a fashion which



appears to be independent of their activating effect on the dark reaction at similar and higher concentrations. In fact, Hill oxidants appear to be the only substances yet studied with the ability to decrease the light reaction without simultaneously decreasing the dark reaction [effect (c) in previous subsection].

All of the above observations suggest that the oxidant is reduced directly at chlorophyll just as might be expected to occur via the mechanism of Linschitz *et al.* (24) if the oxidized chlorophyll could be simultaneously reduced back to its normal state. It might be expected that all substances which require less free energy for their reduction than the minimum amount made available by light at the chlorophyll would be reduced at about the same rate (determined by their rate of arrival at excited chlorophyll molecules) at saturating light intensities. This condition apparently exists at oxidant concentrations below about  $10^{-3}M$  (unpublished results, this laboratory). Competition between oxidants would be governed by their relative affinity for chlorophyll-*a* in the ground state. The wide variety of substances which can serve as Hill oxidants indicates that the reduction process is very general and does not require binding the oxidant to a protein before reduction (as would be expected in a strictly enzymic process).

Turning now to complete photosynthesis, the older evidence as reviewed in Rabinowitch (13) together with the chemiluminescence studies of Strehler *et al.* (88, 89) suggest that carbon-dioxide reduction in photosynthesis occurs at least one step removed from the pigment. If this is assumed to be true, then it would be quite possible that Hill reagents, since they are quite good oxidants, could by-pass some of the intermediates required for normal photosynthesis. Simultaneous measurements on fluorescence and Hill reaction rate might be very useful in elucidating this point.

On the other hand, inhibition by oxidants may be interpreted in just the reverse way. Below inhibiting concentrations oxidants would not successfully compete (by means of a nonuseful reaction) with the natural acceptor and thus prevent the reaction, but at higher concentration the natural acceptor would be by-passed and the light step restricted. Along these lines Kautsky [drawing on Zedlitz' unpublished fluorescence data on the Hill reaction (94)] has proposed a single acceptor for the Hill reaction which always intervenes between chlorophyll and other substances, and which would serve to initiate both oxidation and reduction processes upon excitation. In this scheme the fluorescence of chlorophyll would be regulated only by factors altering the concentration of available acceptor. Reaction with the Hill oxidant would return the acceptor to the form in which it could accept energy from chlorophyll and thus quench chlorophyll fluorescence. Increased light intensity or the presence of those inhibitors which tie up acceptor molecules would be expected to increase fluorescence as observed. Our studies on the Hill reaction indicate that phenylurethane may be an inhibitor of this type since it is distinctly a poison for the Hill reaction in

that it inhibits the light reaction only slightly at concentrations sufficient to almost completely inhibit the dark reaction. Urethanes are usually considered as narcotics for photosynthesis, although Wassink & Kersten (95) found ethylurethane to be a poison for the photosynthesis of certain diatoms. These results may cast some doubt on the proposal that narcotics act by direct contact with chlorophyll [Franck (6)].

Specific oxidant effects with quinone and ferricyanide decrease and probably disappear at low oxidant concentrations (below 0.001M) so that it may be desirable to use measuring techniques (dye reduction, hydrogen ion formation, oxygen polarography, potentiometric methods) which will yield precise results under such conditions.

Mehler (90, 96) and Mehler & Brown (97) have clearly demonstrated by enzyme and mass spectrometer studies that oxygen itself is a Hill reaction oxidant. The oxygen is reduced to peroxide in the process. Oxygen does not appear to compete effectively with ferricyanide and quinone, but rivals chromate in efficiency (unpublished results, this laboratory). Washed chloroplast fragments are themselves reduced to some extent upon illumination. The reduced fragments could be back-titrated, exhibiting two reactions with ferricyanide, one much slower than the other [Gilmour *et al.* (98)]. At least some of the faster reaction sites were present on the surface of the chloroplast fragments so that reactions could occur directly with metal electrodes. While this work only suggests that oxidant reduction takes place at the chloroplast fragment surface, the surface sites could very well account for the ability of fragments to reduce cytochrome-*c* [Mehler (90); Rosenberg & Ducet (99)], a protein molecule which is probably too large to diffuse into grana with the required speed. Determination of maximum obtainable light and dark reactions with this oxidant might establish the positions of reducing centers as either on or in the grana.

Krasnovskii & Kosobutskaya (100) obtained, in a suspension of chloroplast fragments and cytoplasm from bean leaves following illumination, a substance which could then reduce several dyes including safranin and riboflavin in the dark. Illumination increased the quantity of the unknown material slightly. This material may be similar to the sunflower cytoplasm constituent of Spikes *et al.* (101) which was alternately reduced in light and oxidized in the dark but could not reduce substances of positive half-cell potential. The "active reduced compound" of bean leaves appears to resemble more closely an unknown substance (not peroxide) present in sugar-beet-chloroplast fragments even following washing. This material after light or heat treatment can double the normal dark step velocity of the Hill reaction until it is consumed (Bishop, unpublished work, this laboratory).

Further work in this interesting but as yet undeveloped field of the photoreducible substances of chloroplasts has been reported by Davenport & Hill (102), who described a new cytochrome (cytochrome-*f*) in chloroplasts which had a standard potential approximately midway between that of the

oxygen electrode and the usual best estimates for the maximum reducing power of illuminated chloroplasts. Davenport *et al.* (103) also showed that a soluble protein-like factor from the plant cytoplasm was necessary to couple muscle methemoglobin as a Hill oxidant. This substance may represent a natural transfer system between chloroplasts and cytochrome systems. Its connection with the substances mentioned in the preceding paragraph is not known.

The significance of studies on the "maximum" reducing power in the Hill reaction of illuminated chloroplasts is not completely clear. Obviously some such limit exists, but the kinetics of the chloroplast-oxidant reaction should also be studied. Assuming the absence of oxidant effects, recent studies on oxidants generally confirm the older conclusions that illuminated chloroplasts under ordinary conditions cannot significantly reduce substances which have a stronger reducing power than hydrogen [Madowall (104); Wessels & Havinga (105)]. The one principal exception was toluylene blue ( $E_0 = -0.169$  volts at pH 6.5) which gave an electrode potential as high as  $+0.239$  volts upon illumination according to Madowall. Because of the great possibility of artifacts with electrode reactions, it would be desirable to confirm this result in some other way, perhaps by photometric methods.

The so-called "chloride" effect in the Hill reaction as first observed by Warburg has not yet been explained to the satisfaction of all workers in the field. Gorham & Clendenning (106), for example, proposed that chloride and certain other anions actually stimulate the photolysis of water rather than simply prevent light inactivation of the chloroplasts [see Arnon & Whatley (107)]. Increased anion concentration gave higher maximum velocities together with a shift to higher pH of the pH optimum. Gorham & Clendenning (106) also noted that thiocyanate was inhibitory even at low concentrations. Thiocyanate inhibition has been confirmed in this laboratory as part of a series of studies on inhibitors of the Hill reaction. Univalent anions were found to be generally inhibitory but at least two classes of mechanism are represented, both obeying mass law rather than salting-out expressions [Spikes & Lumry (108)]. Univalent cations also inhibit at high concentration. Hagen *et al.* (109) studied the sorption of ions by isolated chloroplasts. Whittingham (110) showed that hydrocyanic acid rather than cyanide ion inhibited the carbon dioxide fixation in photosynthesis presumably by competing with carbon dioxide. Ehrmantraut & Rabinowitch (79) examined the effect of a number of inhibitors on the Hill reaction with intact *Chlorella* and made the interesting observation that malonic acid inhibition occurred which could be prevented by the addition of an equimolar amount of fumarate. We have repeated this using chard chloroplasts. However the results are complex.

As mentioned at the beginning of this section, it has not as yet been possible to develop a satisfactory formal mechanism for the Hill reaction.

We are encouraged to find in our own work, however, that chloroplast fragments from a number of plants and under a wide variety of conditions (pH, light intensity and wave length, oxidant type, temperature, inhibitors, etc.) always follow rectangular hyperbolas in plots of Hill-reaction rate versus light intensity, even up to our highest intensities of 20 joules/cm.<sup>2</sup>-sec. Certain plants, such as sugar beet, prepared in ways which preserved other constituents of the chloroplast did not yield this simple behavior. These facts support the idea that few substances and perhaps few elementary reactions are required to support the Hill reaction.

*Quantum requirements.*—The one-quantum mechanism proposed for algal photosynthesis by Warburg & Burk and their collaborators can be treated only briefly here (111 to 116). A number of attempts to repeat this work have been made in the United States: Brown (117), Brackett (118), and in this laboratory using the Hill reaction (119). None of these have been successful, although investigators using Burk's apparatus have obtained confirmatory results. If the one-quantum results are incorrect, the artifact probably results from the low rate of establishment of gas-exchange steady-states which characterizes Warburg manometers. Calvin *et al.* (1) proposed that the observations result from the non-steady state conditions which exist in a system constantly moving toward a new steady state. Tamiya (120) has observed a multistage growth process in *Chlorella* composed of photosynthesizing and non-photosynthesizing steps which complicates any interpretation of quantum yield with this alga. There still seems to be no completely satisfactory solution to the arguments for and against the four-quantum requirement of photosynthesis. Franck (121) presented rather convincing arguments against such a low requirement based on a summation of the estimated unavoidable energy losses in photosynthesis. Warburg and collaborators continue, however, to measure a four-quantum requirement even at high pH values.

Other quantum-yield studies have been largely concerned with the Hill reaction. Ehrmantraut & Rabinowitch (79) noted requirements for the Hill reaction of *Chlorella* which varied from 10 to 14 depending on the light-intensity measuring device used and on the amount of oxidant (quinone) present. The quantum requirement for photosynthesis with the same culture of algae was about 12, while *Phytolacca americana* chloroplast fragments required 10.6 quanta. No attempt was made to determine the dependence of the quantum requirement on light intensity, but in view of the very high light intensities required to secure light saturation in *Chlorella*, the reported values are probably very close to the minimum for their algal material. In addition to the complications introduced by specific oxidant effects as described earlier, most chloroplast preparations have such low light saturation intensities that it is necessary to extrapolate quantum-yield determinations to zero light intensity for maximum values. This was not done by Ehrmantraut & Rabinowitch.

Wayrynen (119) studied the quantum requirement of the Hill reaction potentiometrically using sugar-beet chloroplasts and a low oxidant concentration. A requirement of  $8.3 \pm 0.3$  quanta (as extrapolated to zero light intensity) at  $675 \mu$  was found. This value was independent of temperature and very nearly independent of pH. The stoichiometric equivalence of oxygen evolved and ferricyanide reduced as originally established (92) has been extended down to the region of  $10^{-4}M$  ferricyanide in the region of concentration used by Wayrynen. This work should be repeated under more anaerobic conditions and with more highly washed chloroplast fragments. Both improvements are expected to reduce the requirement. The quantum requirement rose to a maximum at  $575 \mu$ , and fell again slightly at  $475 \mu$ , the shortest wavelength used. There was no indication of a rapid fall-off at shorter wave lengths as found by Warburg using quinone as an oxidant with spinach chloroplast fragments (122). His observed change from 70 quanta at  $400 \mu$  to 100 at  $644 \mu$  was offered as evidence for a fundamental difference between the Hill reaction and photosynthesis. While such changes may very well exist, even to the extent of differences in the smallest quantum requirement for the two processes, Warburg's high values were obtained at quinone concentrations of  $0.0053M$  which are far into the region where anomalous oxidant effects appear and should be interpreted with caution. Chen (123) very carefully determined the action spectrum for dye reduction by chard chloroplasts and found a large proportionate difference between absorption and action spectra in the  $575 m\mu$  region which agrees with Wayrynen's results (119). No explanation for the energy loss in this region has been established.

#### CARBON DIOXIDE FIXATION

The intermediate processes and compounds in carbon dioxide fixation have been recently reviewed by Calvin *et al.* (1). Significant papers have since appeared however. The formation of the  $C_7$  carbon dioxide acceptor may involve the  $C_6$  sugar ribulose and the  $C_7$  sugar sedoheptulose [Benson *et al.* (124); also (125)]. Uridine diphosphate glucose may be involved in sucrose synthesis [Buchanan *et al.* (126)]. Calvin & Massini (127) have suggested that recently formed carbon dioxide fixation intermediates do not enter the respiratory cycle because  $\alpha$ -lipoic acid (co-pyruvate oxidase) is not present in the necessary oxidized form during illumination. Useful although preliminary kinetic studies have been made on the rate of accumulation of radioactivity in the different intermediates of steady-state photosynthesis (127). Such an approach should permit a much clearer delineation of the sequence of intermediates in carbon dioxide fixation. Clendenning & Gorham (128) re-examined the question of the intracellular localization of the first products of photosynthesis. Assimilated tracer carbon appeared mainly in the cell sap fraction rather than in the chloroplasts. Van Norman & Brown (129), using a recording mass spectrometer, showed that the dis-

crimination for different carbon isotopes in *Chlorella* is several times greater than would be expected for a simple reaction. They showed that  $C^{18}O_2$ ,  $C^{13}O_2$  and  $C^{14}O_2$  were apparently metabolized at the relative rates of 1.00: 0.96: 0.85 [Also see Baertschi (130); Wickman (131)]. Davis (132) reported studies with ultraviolet produced biochemical mutants of *Chlorella* which, although apparently having normal chlorophyll, required reduced carbon for growth.

Vishniac & Ochoa (133, 134) found that illuminated chloroplasts could reduce pyridine nucleotides. Photochemically reduced TPN, in the presence of added enzyme systems, brought about the formation of malate and succinate from carbon dioxide and pyruvate [also see Arnon & Heimbürger (135); Vinogradov *et al.* (136)]. Fager (137) found that cell-free preparations from leaves showed an increased rate of carbon dioxide fixation upon illumination, with most of the carbon dioxide incorporated into phosphoglycerate and phosphopyruvate. Such preparations do not show the Hill reaction. The carbon dioxide incorporation reaction required a cytoplasmic protein fraction soluble in 47.5 per cent acetone and insoluble in 60 per cent acetone (138). Additional papers on carbon dioxide fixation include (139) and (140).

#### MISCELLANEOUS

*Phosphate metabolism and photosynthesis.*—Simonis & Grube (141) found an increase in the trichloroacetic acid soluble phosphorus in *Elodea* leaves illuminated in the presence of carbon dioxide [also see Wintermans & Tjia (142)]. Strehler & Totter (143) reported an ingenious technique using the firefly luminescence reaction for measuring ATP. This technique, which has an ultimate sensitivity of  $10^{-9}$  gm. ATP/ml. was used to demonstrate a marked rise in the ATP concentration of *Chlorella* cells on illumination. Holden (144) reported studies on the fractionation and enzymatic breakdown of some of the phosphorus compounds in chloroplasts. Vishniac & Ochoa (145) demonstrated the coupling of diphosphopyridine reduced by illuminated chloroplasts to the incorporation of inorganic phosphate into ATP by mitochondrial preparation.

*Bacterial photosynthesis.*—The metabolism of photosynthetic bacteria has recently been reviewed by Gest (146). Kamen and co-workers (147, 148, 149) have continued studies on photosynthetic bacteria. They conclude that no carbon dioxide fixation pattern unique to photosynthesis occurs. Gest (150) found the hydrogenase from *Rhodospirillum rubrum* to be very similar to that of *E. coli*. Morita *et al.* (151) showed that the S-shaped photosynthetic rate versus light intensity curves for purple bacteria resulted from photochemical hydrogen evolution during photosynthesis. Larsen (152) isolated new strains of green sulfur bacteria including one new species. The new strains were able to use thiosulfate, tetrathionate and hydrogen as electron donors. Larsen *et al.* (153) found the quantum requirement per molecule of carbon dioxide fixed to be  $10 \pm 1$  for the green bacteria at 732  $m\mu$  regardless

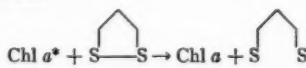
of the electron donor used (thiosulfate, tetrathionate, molecular hydrogen). These results were taken to indicate that the primary photochemical reaction in bacterial photosynthesis, as in the green plants, is the photolysis of water.

*Enzyme systems and cellular structure.*—A number of workers have studied the occurrence and intracellular localization of enzymes which might be involved in photosynthetic reactions (154 to 162).

#### THE FUTURE OF PHOTOSYNTHESIS STUDIES

Progress in certain phases of photosynthesis has been rapid, especially since the discovery of the Hill reaction and the application of the newer tracer techniques. The most effective approach to both Hill reaction and carbon dioxide fixation studies now reduce to careful kinetic investigations. These are difficult to make and even more difficult to interpret, so that we may expect a slower development of these aspects of the over-all process in the future. As yet there exists little but conjecture concerning the dismutation or collection steps in which molecular oxygen is produced. Studies in flashing light of the velocity, fluorescence and chemiluminescence of photosynthetic systems give some promise in this direction, but these present experimental difficulties. Rate studies along this line have not as yet provided information about the latter stages of the light reaction in our laboratory.

The laborious process of developing a formal mechanism of the Hill reaction by means of steady-state and non-steady-state kinetics provides the surest path to future progress. However, one should not discount the past and future importance of direct experimental approaches. For example, Dorough & Calvin (163) studied the carotenoids, which are known to add simple molecules readily across their double bonds, as possible frameworks on which to produce oxygen from water. Following extraction, they examined these pigments for enrichment in  $O^{18}$  after photosynthesis in  $H_2O^{18}$ . The results were inconclusive, but the approach should be developed further. More recently Calvin & Barltrop (164) proposed that a five-membered ring containing two linked sulfur atoms, (a part of the thioctic-acid-containing coenzyme protogen involved in the oxidative decarboxylation of pyruvic acid), is the reactive group we have called the initial acceptor. This group would function as follows:



An analogue of this sulfur compound does appear to participate in a reaction of this kind when photosensitized by zinc tetraphenylporphine. Future developments in this direction are awaited with interest.

Schenck (165 to 168) has presented some new ideas on the thermodynamics of the water oxidation process in photosynthesis which may, with



further experiments, prove important. Uri plans to continue investigation of free radicals in photosynthesis in order to develop a mechanism he has proposed (169). This mechanism is based on recent developments in the light reactions of solvated inorganic ions and resembles the mechanism of Linschitz *et al.* (24). Elucidation of the detailed mechanism of quantum transfer among chlorophyll molecules is progressing rapidly (75, 77). On the other hand, the disagreement among the various groups about the quantum requirement of photosynthesis appears unresolvable. Data obtained by new experimental approaches to this problem in general favor the higher requirements (eight to ten quanta per CO<sub>2</sub> molecule). These results further emphasize the necessity for careful interpretation of the results of conventional manometric experiments.

Developments in artificial photosynthesis, in particular the studies on light photooxidation of water in the presence of ceric ion [Heidt (170)], should be carefully examined by workers on the natural reaction.

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# MICROWAVES AND NUCLEAR RESONANCE<sup>1</sup>

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This article discusses the subject indicated by the title under three headings. Part I is a reasonably complete review of progress in microwave spectroscopy since the appearance of Wilson's article in the *Annual Review of Physical Chemistry*, Volume 2. Part II is a review, also meant to be reasonably complete, of the closely allied field of direct quadrupole spectroscopy. Part III is a review of some of the chemically interesting applications of nuclear magnetic resonance absorption. Because of limitations of space, Part III is quite brief and the related interesting subjects of paramagnetic and ferromagnetic resonance and microwave dispersion in solids and liquids in the absence of external fields, could not be discussed at all.

## I. MICROWAVE SPECTROSCOPY

In the period covered by this review two conferences on radiofrequency spectroscopy have been held which have resulted in published review articles on special topics in microwave spectroscopy. At the Amsterdam conference papers were given and later published in *Physica* by Townes (125), Freymann (29), Jen (53), and by Nielsen (91). The New York Academy of Sciences Conference held in November, 1951, resulted in a monograph which includes reviews by Townes (123) Geschwind (31), Gordy (39), Mays (79), Strandberg (118), Beringer (10), Jen (52), Lyons (73), Hughes (49), Smith (115), Cohen (15), Dailey (21), and by Wilson (138). A number of additional reviews by Raev (94), Martin (78), Lyons (74), Klages (64), Hönerjäger (47), Bleaney (13), Maier (77), and Freymann, LeBot & LeMontagner (28) have also appeared.

*Experimental developments.*—Several groups, because of their interest in studying small, hyperfine structure effects, have been working in the direction of improved high resolution spectrometers. Geschwind (31) has described his balanced bridge spectrometer with superheterodyne detection in which line widths of about 100 kc. are obtained. This paper includes a good discussion of the factors contributing to line width and of the principles of spectrometer design. Newell & Dicke (90) have described a "Stark reflection" spectrometer for reducing the Doppler broadening with which line widths of some 3.5 kc. have been obtained at the expense of a very considerable reduction in sensitivity. Johnson & Strandberg (58) have experimented with a beam system spectrometer for reduction of Doppler broadening, but because of poor sensitivity were unable to observe lines narrower than 20 kc.

<sup>1</sup> The survey of the literature pertaining to this review was completed in December, 1952.



Progress in extending the applicability of microwave spectrometers to high boiling, reactive, and unstable molecules has been reviewed by Mays (79). Rueger, Lyons & Nuckolls (101) have described a Stark absorption cell which can be operated at temperatures up to 250°C. and which was especially designed to permit thorough outgassing of the cell when used with vapors which tend to absorb on the exposed metal surfaces of the wave guide. Perhaps the most spectacular instrument of this type to be developed is the spectrometer used by Stitch, Honig & Townes (117) to observe the spectra of CsCl, KCl, TeCl, and NaCl at temperatures up to 800°C. Special features of this instrument include double vacuum windows, permitting considerable simplification in the design of the inner high temperature windows and a Stark electrode which is supported in a vertical position by small forsterite beads along its edges.

Smith *et al.* (114) have developed effective methods of dealing with highly reactive fluorine compounds in the microwave spectrometer. The problem of the detection of the spectra of free radicals has occupied a number of laboratories. This work, as summarized by Mays (79), is mostly a series of failures. However, Schawlow, Sanders & Townes (124) have recently obtained a spectrum for the OH radical. The radicals were produced by an electrodeless electric discharge in water vapor, pumped through the wave guide, and detected by Zeeman modulation. The observed lines had a signal to noise ratio of approximately 300 for an estimated OH radical concentration of 0.5 per cent. The absorption cell was made entirely of glass since metal surfaces strongly catalyzed the recombination of the OH radicals.

Gordy (39) has reviewed the work of his group on spectroscopy above 60 kmc. High frequency spectra for HCN obtained by the Columbia group are described by Nethercot, Klein & Townes (89).

A spectrometer suitable for the measurement of absolute values of the absorption coefficient and for studies on line widths at higher pressures has been described by Artman (8). The method consists essentially of determining the  $Q$  of a very large nonresonant cavity in the presence and absence of the absorbing gas. Other references dealing primarily with apparatus and experimental techniques are (97) and (101).

*Determination of molecular structure.*—A few papers have appeared amplifying portions of the theoretical background used for the interpretation of microwave spectra. Wilcox & Goldstein (135) have measured relative intensities and determined statistical weights to demonstrate the presence or absence of a plane of molecular symmetry. Lide (69) has discussed the calculation of rotational line strengths in slightly asymmetric rotor molecules. Mizushima (84) has described a method for calculation of the Stark effect for an asymmetric rotor in the presence of nuclear quadrupole hyperfine structure. With Ito (86) he has presented a method for calculating the nuclear hyperfine structure patterns for  $XYZ_3$  molecules when  $Z$  has a spin greater than  $\frac{1}{2}$ .

Several authors have tried to simplify calculations of centrifugal distortion effects so that they may be taken account of in the analysis of spectra. One of the more interesting of these papers is that of Kivelson & Wilson (63). Hillger & Strandberg (46) have considered centrifugal distortion effects in the spectrum of HDS. Bird (12) has studied power saturation phenomena which might prove useful in spectral analysis.

A number of papers discussing the effects of various small perturbations have appeared. Among these are the paper of Weatherly & Williams (129) on l-doubling in KCN and DCN, and of Van Vleck (127) and Good *et al.* (38) on new hyperfine structure effects in  $\text{NH}_3$ .

Table I is a list of molecules whose microwave spectra have been studied

TABLE I  
MOLECULES STUDIED WITH MICROWAVE SPECTROSCOPY

Formula	Compound	Reference
$\text{NH}_3$	ammonia	(16, 17, 131, 133) (38, 92, 93, 102)
OCS	carbonyl sulfide	(55, 56, 121)
$\text{N}_2\text{O}$	nitrous oxide	(55, 121)
HCN	hydrogen cyanide	(89, 122, 129)
BrCN	cyanogen bromide	(120)
$\text{Na}^{23}$	sodium	(108)
Cs	cesium	(95)
H	hydrogen	(23, 27, 66, 67, 128)
CsCl	cesium chloride	(117)
NaCl	sodium chloride	(117)
$\text{SbH}_3$	stibine	(72)
$\text{AsH}_3$	arsine	(72)
$\text{PH}_3$	phosphine	(72)
$\text{GeF}_2\text{Cl}$	trifluorochlorogermane	(6)
$\text{NO}_2$	nitrogen dioxide	(88)
$\text{CF}_3\text{C}\equiv\text{H}$	trifluoro-methyl acetylene	(7, 109, 110)
$\text{CH}_3\text{SH}$	methyl mercaptan	(48, 51, 96)
$\text{PCl}_3$	phosphorous trichloride	(60, 62)
$\text{AsCl}_3$	arsenic trichloride	(60, 62)
$\text{SbCl}_3$	antimony trichloride	(60, 62)
$\text{PF}_3$	phosphorous trifluoride	(56, 60)
$\text{NF}_3$	nitrogen trifluoride	(56, 60)
$\text{AsF}_3$	arsenic trifluoride	(60)
$\text{O}_2$	oxygen	(3, 4, 5, 11, 37)
NOF	nitrosyl fluoride	(75, 76)
NOCl	nitrosyl chloride	(98)
HCOOH	formic acid	(99)
$\text{CH}_3\text{Cl}$	methyl chloride	(82, 111, 112)

TABLE I—Continued

Formula	Compound	Reference
CH <sub>3</sub> Br	methyl bromide	(82, 111, 112)
CH <sub>3</sub> I	methyl iodide	(82, 111, 112)
COF <sub>2</sub>	carbonyl fluoride	(114)
CO	carbon monoxide	(56)
POF <sub>3</sub>	phosphorous oxyfluoride	(44, 56, 137)
CH <sub>3</sub> F	methyl fluoride	(56)
PSF <sub>3</sub>		(44, 56, 137)
CH <sub>3</sub> C CH	methyl acetylene	(56)
CH <sub>3</sub> OH	methyl alcohol	(14, 50)
CH <sub>3</sub> NH <sub>2</sub>	methylamine	(71)
H <sub>2</sub> Si Cl	chlorosilane	(80)
H <sub>2</sub> Ge Cl	chlorogermane	(80)
H <sub>2</sub> Si Br	bromosilane	(80)
H <sub>2</sub> Ge Br	bromogermane	(80)
HCBF <sub>3</sub>	bromoform	(65, 136)
D <sub>2</sub> O	heavy water	(9)
CH <sub>2</sub> Cl <sub>2</sub>	methylene chloride	(87)
CH <sub>3</sub> COCH <sub>3</sub>	acetone	(130)
CH <sub>3</sub> C≡CBr	bromomethyl acetylene	(107)
CH <sub>3</sub> C≡CI	iodomethyl acetylene	(107)
H <sub>2</sub> C=C=O	ketene	(58)
HCCL <sub>3</sub>	chloroform	(35)
HCF <sub>3</sub>	fluoroform	(35)
CH <sub>3</sub> CCl <sub>3</sub>	methyl chloroform	(35)
CF <sub>3</sub> Br	trifluoromethyl bromide	(106)
CF <sub>3</sub> I	trifluoromethyl iodide	(106)
CF <sub>3</sub> CN	trifluoroacetonitrile	(106)
CF <sub>3</sub> SF <sub>6</sub>		(61)
B <sub>5</sub> H <sub>11</sub>	pentaborane	(48)
ReO <sub>3</sub> Cl	rhenum trioxy-chloride	(1)
C <sub>4</sub> H <sub>4</sub> NH	pyrrole	(135)
PSCL <sub>3</sub>		(137)
POCL <sub>3</sub>		(137)
SO <sub>2</sub> F <sub>2</sub>	sulfuryl fluoride	(30)
C <sub>2</sub> H <sub>5</sub> SnH <sub>3</sub>	methyl stannane	(69)
SiF <sub>3</sub> H	trifluorosilane	(105)
SiF <sub>2</sub> Cl	trifluorochlorosilane	(105)
SiF <sub>2</sub> Br	trifluorobromosilane	(105)
SiF <sub>2</sub> CH <sub>3</sub>	trifluoromethylsilane	(105)
SO <sub>2</sub>	sulfur dioxide	(113)
C <sub>2</sub> H <sub>4</sub> O	ethylene oxide	(20)
C <sub>2</sub> H <sub>4</sub> S	ethylene sulfide	(20)
HDS	hydrogen sulfide	(46)

in the period covered by this review. More or less complete structural information has been obtained for some of them. If the structural analysis involved the assumption of no more than one parameter (indicated by parentheses) the bond angles and bond distances will be found in Table II. The limits of error are those indicated by the authors and may be seen to vary considerably.

TABLE II  
STRUCTURAL DATA

Formulas	Parameters	Reference
PH <sub>2</sub> D	$r = 1.419\text{\AA}$ $\theta = 93.5$	(72)
AsH <sub>2</sub> D	$r = 1.523\text{\AA}$ $\theta = 92.0$	(72)
SbH <sub>2</sub> D	$r = 1.712\text{\AA}$ $\theta = 91.5$	(72)
HCN	$d_{\text{CH}} = 1.0646\text{\AA}$ $d_{\text{CN}} = 1.1562$	(89)
CF <sub>3</sub> C CH	$\angle \text{FCF}$ (tetrahedral) ( $d(\text{C}=\text{C}) = 1.20\text{\AA}$ ) ( $d(\text{CH}) = 1.056\text{\AA}$ ) $d(\text{CF}) = 1.330\text{\AA}$ $d(\text{C}-\text{C}) = 1.493\text{\AA}$	(7)
GeF <sub>3</sub> Cl	$\angle \text{FGeF}$ $107.7 \pm 1.5^\circ$ $d_{\text{GeF}} = 1.688 \pm 1.017\text{\AA}$ $d_{\text{GeCl}} = 2.067 \pm 0.005\text{\AA}$	(6)
COH	$110^\circ 15'$ ( $\text{O}-\text{H} = .958\text{\AA}$ ) $\text{C}-\text{O} = 1.421\text{\AA}$	(14)
NOCl	(component) $\mu_{\text{A}} = .04$	(98)
CsCl	$\text{Cs}-\text{Cl} = 2.9041 \pm .0003\text{\AA}$	(117)
NaCl	$\text{Na}-\text{Cl} = 2.3606 \pm .0003\text{\AA}$	(117)
SO <sub>2</sub>	$\text{S}-\text{O} = 1.432\text{\AA}$ $\angle \text{O}-\text{S}-\text{O} = 119^\circ 2.1'$	(19)
C <sub>2</sub> H <sub>4</sub> O	$\text{C}-\text{C} = 1.472$ $\text{C}-\text{O} = 1.436$ $\text{C}-\text{H} = 1.082$ $\angle \text{H}-\text{C}-\text{H} = 116^\circ 41'$ $\angle \text{H}_2\text{C}-\text{C} = 159^\circ 25'$ $\angle \text{C}-\text{O}-\text{C} = 61^\circ 24'$ $\angle 1/2 \text{ H}_2\text{CC}-1/2 \text{ H}_2\text{CO} = 70^\circ 40'$	(20)
C <sub>2</sub> H <sub>4</sub> S	$\text{C}-\text{C} = 1.492$ $\text{C}-\text{S} = 1.819$ $\text{C}-\text{H} = 1.078$ $\angle \text{H}-\text{C}-\text{H} = 116^\circ 0'$ $\angle \text{H}_2\text{C}-\text{C} = 151^\circ 43'$ $\angle \text{C}-\text{S}-\text{C} = 65^\circ 48'$ $\angle 1/2 \text{ H}_2\text{CC}-1/2 \text{ H}_2\text{CO} = 4^\circ 37'$	(20)
SO <sub>2</sub> (Sirvetz)	$\text{S}-\text{O} = 1.432$ $\angle \text{OSO} = 119.53^\circ$	(113)
NOF	$\text{N}-\text{F} = 1.52$ $\text{N}-\text{O} = 1.13$ $\angle \text{ONF} = 110^\circ$	(74)
CF <sub>3</sub> C CH	$\angle \text{FCF} = 107.5 \pm 1^\circ$ $\text{C}-\text{C} = 1.464 \pm .02$ $\text{C}-\text{F} = 1.335 \pm .01$ $\text{C}-\text{H} = 1.056 \pm .005$ $\text{C}=\text{C} = 1.201 \pm .002$	(109, 110)
CH <sub>3</sub> SnH <sub>3</sub>	(tetrahedral) ( $\text{C}-\text{H} = 1.090$ ) $\text{C}-\text{Sn} = 2.143 \pm .002$ $\text{Sn}-\text{H} = 1.700 \pm .015$	(70)
SO <sub>2</sub> F <sub>2</sub>	$\text{S}-\text{O} = 1.370 \pm .01$ $\text{S}-\text{F} = 1.570 \pm .01$ $\angle \text{O}-\text{S}-\text{O} = 129^\circ 38' \pm 30'$ $\angle \text{F}-\text{S}-\text{F} = 92^\circ 47' \pm 30'$	(30)
POF <sub>3</sub>	$\text{P}-\text{O} = 1.45 \pm .03$ $\text{P}-\text{F} = 1.52 \pm .02$ $\angle \text{FPF} = 102.5^\circ \pm 2^\circ$	(137)
PSF <sub>3</sub>	$\text{P}-\text{S} = 1.87 \pm .03$ $\text{P}-\text{F} = 1.53 \pm .02$ $\angle \text{F}-\text{P}-\text{F} = 100.3^\circ \pm 2^\circ$	(137)
POCl <sub>3</sub>	$\text{P}-\text{O} = 1.45 \pm .03$ $\text{P}-\text{Cl} = 1.99 \pm .02$ $\angle \text{Cl}-\text{P}-\text{Cl} = 103.6^\circ \pm 2^\circ$	(137)
PSCl <sub>3</sub>	$\text{P}-\text{S} = 1.85 \pm .02$ $\text{P}-\text{Cl} = 2.02 \pm .01$ $\angle \text{Cl}-\text{P}-\text{Cl} = 100.5^\circ \pm 1^\circ$	(137)
ReO <sub>3</sub> Cl	$\text{Re}-\text{Cl} = 2.230 \pm .004$ $\text{Re}-\text{O} = 1.761 \pm .003$ $\angle \text{Cl}-\text{Re}-\text{O} = 108^\circ 20' \pm 1^\circ$	(1)

TABLE II—Continued

Formulas	Parameters	Reference
PSF <sub>3</sub> (Hawkins)	P-S = 1.86 P-F = 1.63 $\angle$ F-P-F = 100°	(44)
POF <sub>3</sub> (Hawkins)	P-O = 1.48 P-F = 1.52 $\angle$ F-P-F = 106°	(44)
CHF <sub>3</sub>	C-H = 1.098 C-F = 1.332 $\angle$ F-C-F = 108°48'	(35)
CHCl <sub>3</sub>	C-H = 1.073 C-Cl = 1.767 $\angle$ Cl-C-Cl = 110°24'	(35)
CH <sub>2</sub> Cl	C-H = 1.101 C-Cl = 1.7815 $\angle$ H-C-H = 110°13'	(87)
CH <sub>3</sub> CO	C-H = 1.075 ± .01 C-O = 1.16 ± .1 C-C = 1.31 ± .1	(57)
CH <sub>3</sub> Br	C-H = 1.100 C-Br = 1.9393 $\angle$ H-C-C = 111°0'	(82)
CH <sub>3</sub> I	C-H = 1.102 C-I = 2.1389 $\angle$ H-C-H = 111°2'	(82)
CH <sub>2</sub> Cl <sub>2</sub>	C-Cl = 1.7724 ± .005 C-H = 1.068 ± .005 $\angle$ Cl-C-Cl = 111°41' ± 1'	(87)
CHBr <sub>3</sub>	C-H = 1.07 ± .01 C-Br = 1.930 ± .003 $\angle$ Br-C-Br = 110°48' ± 16'	(136)
SiH <sub>3</sub> Cl	Si-Cl = 2.048 ± .004 Si-H = 1.50 ± .03 $\angle$ H-Si-H = 110°57' ± 90'	(80)
GeH <sub>3</sub> Cl	Ge-Cl = 2.148 ± .003 Ge-H = 1.52 ± .03 $\angle$ H-Ge-H = 110°54' ± 90'	(80)
CF <sub>3</sub> Cl	C-F = 1.328 ± .005 C-Cl = 1.740 ± .018 ( $\angle$ F-C-F = 108° ± 1°)	(106)
CF <sub>3</sub> Br	C-F = 1.330 ± .005 C-Br = 1.908 ± .108 ( $\angle$ F-C-C = 108° ± 1°)	(106)
PCl <sub>3</sub>	P-Cl = 2.043 ± .003 $\angle$ Cl-P-Cl = 100°7' ± 20'	(60)
AsCl <sub>3</sub>	As-Cl = 2.161 ± .004 $\angle$ Cl-As-Cl = 98°25' ± 30'	(60)
SbCl <sub>3</sub>	Sb-Cl = 2.325 ± .005 $\angle$ Cl-Sb-Cl = 99° ± 1.5°	(60)
SiF <sub>3</sub> H	(Si-H = 1.550 ± .05) Si-F = 1.561 ± .002 $\angle$ F-Si-F = 108°6' ± 4'	(105)
SiF <sub>3</sub> Cl	Si-F = 1.56 ± .005 Si-Cl = 1.983 ± .018 ( $\angle$ F-Si-F = 108°6')	(105)
SiF <sub>3</sub> Br	Si-F = 1.560 ± .005 Si-Br = 2.147 ± .02 ( $\angle$ F-Si-F = 108°6')	

*Valence information.*—The significance of the results of microwave spectroscopy to valence theory has been reviewed by Wilson (138). The scope of the information to be obtained from the analysis of nuclear quadrupole hyperfine structure has been greatly expanded by the development of direct quadrupole spectroscopy. This information will be discussed under that heading in this review. The work of Gwinn and co-workers (20, 87) on molecules with bent bonds is of great interest. Their experiments seem to confirm the existence of such bonds in methylene chloride as well as such small ring systems as ethylene oxide and ethylene sulfide.

*Dipole moments.*—The dipole moments measured by the analysis of Stark effects in microwave spectra during the period covered by this review are given in Table III. The determination of two components of the dipole moment by Magnuson (75) for nitrosyl fluoride represents one of the few occasions in which such a complete analysis has been possible. Efforts to relate the dipole moment to the valence structures of a given molecule have been

TABLE III  
 DIPOLE MOMENTS FROM MICROWAVE SPECTROSCOPY

Molecule	Dipole Moment	Reference
SO <sub>2</sub>	1.59 ± 0.01	(19)
C <sub>2</sub> H <sub>4</sub> O	1.88	(20)
C <sub>2</sub> H <sub>4</sub> S	1.84	(20)
CF <sub>3</sub> C≡CH	2.34	(109)
CH <sub>3</sub> SH	1.26 ± .05	(104)
NOF	1.81	(75)
PH <sub>3</sub> D	0.55 ± 0.01	(72)
AsH <sub>3</sub> D	0.22 ± 0.02	(72)
Sb H <sub>3</sub> D	0.116 ± 0.003	(72)
CH <sub>3</sub> OH	$\mu_{\parallel} = 0.893$ $\mu_{\perp} = 1.435 \times 10^{-18}$ esu	(14)
SO <sub>2</sub> F <sub>2</sub>	0.228	(30)
B <sub>3</sub> H <sub>11</sub>	2.13 ± .04	(48)
PSF <sub>3</sub>	.633 ± .02	(44)
POF <sub>3</sub>	1.69 ± .05	(44)
CH <sub>3</sub> CO	1.45	(57)
CH <sub>2</sub> Cl <sub>2</sub>	1.62 ± .02	(87)
SiH <sub>3</sub> Cl	1.303 ± .01	(80)
GeH <sub>3</sub> Cl	2.124 ± .02	(80)
CH <sub>3</sub> Br	1.797 ± .015	(80)
SiH <sub>3</sub> Br	1.32 ± .03	(80)
CH <sub>3</sub> NH <sub>2</sub>	1.27	(71)

discouraged by Robinson (96) and Coulson (18), who have pointed out the complicated nature of the dependence of the dipole moment on the type of valence bonding present.

*Determination of nuclear properties.*—Microwave measurements of nuclear masses, spins, magnetic dipole moments and electric quadrupole moments have aided in testing the predictions of nuclear shell theory. This subject has been reviewed by Schawlow (103). In the period covered by this review microwave investigators have determined nuclear masses for S<sup>35</sup> (32, 134), S<sup>32</sup>, S<sup>33</sup>, S<sup>34</sup>, S<sup>36</sup>, Ge<sup>70</sup>, Ge<sup>72</sup>, Ge<sup>74</sup>, Ge<sup>7</sup> (32); spins for Se<sup>79</sup> (43) and O<sup>18</sup> (83); a magnetic dipole moment for S<sup>33</sup> (25); and electric quadrupole moments for Se<sup>79</sup> (43) Ge<sup>70</sup>, Ge<sup>72</sup>, Ge<sup>74</sup>, Ge<sup>76</sup> (81), O<sup>17</sup> (34), Cl<sup>35</sup>, and Cl<sup>37</sup> (33). Gunther-Mohr, Geschwind & Townes (42) have studied the polarization of the nucleus in different molecules.

*Hindered internal rotation.*—The contributions of microwave spectroscopy to the problem of internal torsion have been reviewed by Dailey (21). The molecule studied in greatest detail is methyl alcohol. The combined experimental work of Hughes, Good & Coles (50) and theoretical work of Den-

nison and co-workers (14) has resulted in a rather complete analysis. The barrier to internal rotation in methanol is therefore known with greater precision and reliability than for any other molecule. Additional references which discuss hindered rotation effects are Kisliuk & Silvey's discussion of the spectrum of  $\text{CF}_3\text{SF}_6$  (61), articles by Sheridan & Gordy on  $\text{SiF}_3\text{CH}_3$  (105), and by Lide (69) on methylstannane and methyl amine (71).

*Chemical analysis.*—Hughes (49) has written a discussion of the possible analytical applications of microwave spectroscopy. Weber & Laidler (132), using a straight absorption type spectrometer have used microwave spectra for analytic purposes in studying the kinetics of the heterogeneous  $\text{NH}_3$ — $\text{D}_2$  exchange.

Southern *et al.* (116) have used a Stark modulation spectrometer to determine the ratio of  $\text{N}^{15}$  to  $\text{N}^{14}$  in ammonia and the ratio of  $\text{C}^{13}$  to  $\text{C}^{12}$  in  $\text{ClCN}$ . They measured the observed height of the spectral line above the peak of the displaced Stark components eliminating base line errors. The peak ratios for  $\text{N}^{15}/\text{N}^{14}$  were found to vary as a function of time and of the tuning of the microwave components. Errors from this source were avoided by using a calibration curve of  $\text{N}^{15}/\text{N}^{14}$  peak ratios plotted against the percentage of  $\text{N}^{15}$  in standard samples. In the concentrations range of 0.38 to 4.5 per cent  $\text{N}^{15}$  they were able to reduce their analytical error to approximately three per cent and for  $\text{C}^{13}$  concentrations of from 1.1 to 10 per cent an average error of less than 2 per cent was obtained.

*Zeeman effect.*—Jen (52) has reviewed Zeeman effect experiments in microwave spectroscopy. The use of microwave techniques to determine nuclear magnetic moments is only occasionally of special advantage. However, it is possible to determine molecular magnetic moments which should shed some light on the valence structure of molecules. Eshbach & Strandberg (26) have discussed the theoretical calculation of rotational magnetic moments of molecules. Beringer (10) has discussed microwave resonance absorptions in paramagnetic gases which do not involve pure rotational transitions. Beringer & Castle (11) have published a study of the magnetic resonance spectrum of  $\text{O}_2$ .

*Pressure broadening.*—Line width phenomena in microwave spectroscopy have been reviewed by Smith (115). The earlier extensive work on line widths in the inversion spectrum of ammonia has been supplemented by the work of a number of investigators on line widths for  $\text{O}_2$  (4, 8, 37). Hill & Smith (45), Weber (131), and Potter, Bushkovitch & Rouse (93) have studied ammonia-foreign gas mixtures. The nature of the intermolecular forces giving rise to pressure broadening has been discussed by Mizushima (85) and Artman (8). The careful work of Artman on  $\text{O}_2$  seems to establish that Anderson's theoretical approach (2) is essentially correct but needs to be extended to consider exchange forces. The quadrupole forces emphasized by Mizushima seem to lead to an incorrect dependence of line width on  $K$  for  $\text{O}_2$ .



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## II. DIRECT QUADRUPOLE SPECTROSCOPY

An important new branch of radiofrequency spectroscopy was opened up by Dehmelt & Krüger (8) when they observed direct nuclear quadrupole transitions for chlorine in solid *trans*-dichlorethylene. These transitions arise as follows: When a solid sample containing appropriate nuclei is placed in a suitably oriented alternating magnetic field, magnetic dipole transitions occur when the frequency of the field is equal to a transition frequency. The quadrupole energy levels involved may be described in certain simple cases by

$$E_q = \frac{eQq_{ss}}{4I(2I+1)} [3m_I - I(I+1)]$$

where  $eQq_{ss}$  is the nuclear quadrupole coupling constant,  $I$  is the nuclear spin and  $m_I$  is the projection of  $I$  along an axis fixed in space. The selection rule for these transitions is  $\Delta m_I = \pm 1$ . The resulting transition frequencies for chlorine nuclei are  $\nu = eQq/2$ . The same energy levels, arising from the interaction of the nuclear electric quadrupole moment with the gradient of the electric field due to the other charged particles in the same molecule, are responsible for the nuclear quadrupole hyperfine structure in microwave spectra.

This subject has been reviewed by Livingston (16), Kopfermann (13), and by Dailey (3).

*Experimental developments.*—Spectrometers employing superregenerative oscillators were used originally by Dehmelt & Krüger to observe quadrupole resonances for chlorine and bromine (8), and iodine (9) compounds. In these spectrometers the samples are placed in the coil of the tank circuit of the superregenerative oscillator which is frequency modulated by a vibrating condenser. A change in the output amplitude of the oscillator indicates when the frequency of the oscillator is swept through the resonant frequency of the direct quadrupole transition. The output signal is studied with an

oscilloscope after passing through a detector and a low frequency amplifier. Energy from a frequency meter is mixed with the oscillator energy and the resulting pips superimposed on the absorption pattern in order to measure resonant frequencies accurately.

Livingston (16) has described a simple regenerative oscillator used for detecting quadrupole resonances. This is a modification of a circuit developed by Hopkins (12) for nuclear magnetic resonance experiments. Watkins (25) has described a spectrometer (22) employing magnetic modulation and a phase sensitive detector. Dean (4) has also described an improved spectrometer.

*Valence information.*—The values of  $eQq$  obtained in direct quadrupole spectroscopy are of value in indicating the nature of the valence bonds in the molecule just as are the similar quantities derived from hyperfine structure in microwave spectroscopy. In addition they are influenced by solid state effects as pointed out by Townes & Dailey (23). One such striking effect was the intermolecular covalent bonding found in crystalline iodine.

Gordy (I-40) has surveyed the published values of  $eQq$  obtained by both direct quadrupole spectroscopy and microwave spectroscopy and has obtained an interpretation of them which differs in some respects with that of Townes & Dailey (23).

Values of  $eQq$  found by the techniques of direct quadrupole spectroscopy are given in Table IV. In order to separate the solid state and intramolecu-

TABLE IV  
QUADRUPOLE COUPLING CONSTANTS DETERMINED BY DIRECT  
QUADRUPOLE SPECTROSCOPY

Molecule	$eQq$	Reference
Cl <sup>35</sup> Resonances		
Cl <sub>2</sub>	-108.5 Mc.	(17)
CH <sub>3</sub> Cl	-68.40	(18)
CH <sub>2</sub> Cl <sub>2</sub>	-72.47	(18)
CHCl <sub>3</sub>	-76.98	(18)
CCl <sub>4</sub>	-81.85	(18)
CHF <sub>2</sub> Cl	-70.50	(18)
CF <sub>3</sub> Cl	-77.58	(18)
CHFCl <sub>2</sub>	-73.53	(18)
CF <sub>2</sub> Cl <sub>2</sub>	-78.16	(18)
CFCl <sub>3</sub>	-79.63	(18)
CF <sub>2</sub> BrCl	-77.35	(18)
Cl <sub>2</sub>	-108.95	(18)
CH <sub>3</sub> CHCl	-67	(10)
(CH <sub>3</sub> ) <sub>2</sub> N <sub>4</sub>	-6.6	(26)
BrCN	-5.0	(26)
ICN	-5.1	(26)
SOCl <sub>2</sub>	-64.0	(20)
POCl <sub>3</sub>	-57.90	(20)

TABLE IV—Continued

Molecule	$eQq$	Reference
$C_6H_5Cl$	-69.24	(20)
$p\text{-}C_6H_4Cl_2$	-68.5	(24)
$SbCl_3$	-40.8	(24)
	-38.4	(24)
$NaClO_3$	-60.0	(24)
$KClO_3$	-56.8	(24)
$CH_2Cl_2$	-72.0	(24)
$m\text{-}NO_2C_6H_4Cl$	70	(5)
$m\text{-}Cl_2C_6H_4$	69.5	(5)
$C_6H_5Cl$	68.5	(5)
$O\text{-}NO_2C_6H_4Cl$	73.5	(5)
$O\text{-}Cl_2C_6H_4$	70.5	(5)
$p\text{-}Cl_2C_6H_4$	69.0	(5)
$p\text{-}ClC_6H_4OH$	69.5	(5)
$p\text{-}NH_2C_6H_4Cl$	68.5	(5)
<i>trans</i> $CHCl=CHCl$	-70.8	(8)
<i>trans</i> $CHI=CHI$	-1847	(6)
$CH_3CCl_3$	-76.30	(19)
$CH_3CHCl_2$	-71.22	(19)
$CH_3CH_2Cl$	-65.97	(19)
$(CH_3)_2CHCl$	-64.14	(19)
$(CH_3)_3CCl$	-62.39	(19)
$CCl_3CCl_3$	-81.58	(19)
$CCl_3CHCl_2$	-79.91	(19)
	-77.74	
$CH_3Cl\ CH_2Cl$	-68.88	(19)
$CH_3CH_2CH_2Cl$	-66.39	(19)
$C_2H_5(CH_2)_2CCl$	-61.92	(19)
$CH_2Cl\ CHCl\ CH_2Cl$	-69.69	(19)
$CH_3FCI$	-67.60	(19)
$I^{127}$ Resonances		
$CH_3I$	-1753	(6)
$ICN$	-2549	(6)
$ICl$	-3037	(6)
$SnI_4$	-1363	(6)
$I_2$	-2140	(6)
$Br^{79}$ Resonances		
$CH_3Br$	-528.9	(8)
$Br_2$		(7)
$Sb$ Resonances		
$SbCl_3$		(9)
$As$ Resonance		
$As_4O_6$		(15)
$Cu$ Resonance		
$Cu_2O$		(15)
$Cu(CN)_2$		(15)

lar influences on  $eQq$  it is necessary to have a value of  $eQq$  obtained, for the isolated molecule in the gaseous state, from microwave spectroscopy. There is good, rough agreement between values of  $eQq$  measured in the solid and in the vapor but molecules which involve bonds with partial ionic character usually form bonds in the solid which are more ionic than those formed in the gas. When data are not available for the gas it is still frequently possible to reveal striking chemical effects from a qualitative comparison of solid state values of  $eQq$  for a series of similar chemical compounds. The assumption made is that crystal structure effects are small and do not vary greatly from one molecule to the next in the series.

A number of such studies have been made. Livingston has studied the substituted methanes (17) and some aliphatic chlorine compounds (18). In the halogen substituted methanes the observed changes were explained as arising from two opposing effects. The replacement of H by a halogen causes the C—Cl bond to become less ionic. In the case of F, structures such as  $F-C \equiv Cl^+$  become important. In the aliphatic chlorine compounds the ionic character of the C—Cl bond increases with the substitution of  $CH_3$  for H.

Wilson (I-138) has demonstrated a correlation of the  $eQq$  for various substituted chlorobenzenes with Hammett's sigma factor (11) for these molecules. Presumably both  $eQq$  and the sigma factor are similarly affected by a charge displacement in the molecule due to the substituent group.

*Nuclear information.*—The values of  $eQq$  obtained by direct quadrupole spectroscopy are potential sources of information on nuclear electric quadrupole moments. Accurate evaluation of  $eq$  has proved difficult for molecules in the solid state. It is still possible, however, to determine with considerable accuracy the ratio of quadrupole moments for two nuclei. This has been done by Livingston (20) and by Wang *et al.* (24) for the ratio of the quadrupole moments of  $Cl^{35}$  and  $Cl^{37}$  in a variety of compounds. Small effects due to molecular environment were observed and attributed to zero point vibrational effects and a small nuclear polarization.

*Theoretical information.*—Energy levels due to nuclear orientation have been discussed by Bayer (1), Bersohn (2), Dehmelt & Krüger (8), and by Pound (21). Krüger (14) and Bersohn (2) have presented the theory of the Zeeman effect in direct quadrupole spectroscopy and have shown that it permits the determination of all of the principal components of the quadrupole tensor as well as the orientation of the principal axes of the molecule with reference to the crystal axes.

## II. DIRECT QUADRUPOLE SPECTROSCOPY

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### III. NUCLEAR MAGNETIC RESONANCE

An introduction to the subject of nuclear magnetic resonance and a review of work to 1950 has been given by Pake (26). These experiments are designed to determine the energy of orientation of a nuclear magnetic moment in an external magnetic field. The nuclear magnetic moment  $\mu$  is equal to  $gI\mu_0$ , where  $\mu_0$  is the nuclear magneton,  $I$  is the nuclear spin and  $g$  is the gyromagnetic ratio; a number characteristic of a given nuclear species in a given nuclear energy state. The potential energy  $U$  of a nucleus possessing a nuclear magnetic moment  $\mu$  in a magnetic field  $H$  is

$$U = -\mu \cdot H.$$

A nucleus having a spin of  $I$  will have  $2I+1$  values of the projection of  $\mu$  along the direction of the external field and will therefore have  $2I+1$  energy levels characterized by the magnetic quantum number  $m$ . In nuclear magnetic resonance transitions the selection rule is  $\Delta m = \pm 1$ . Therefore the observed resonant frequencies are given by

$$\nu = \frac{gH}{h} \mu_0$$

where  $h$  is Planck's constant.

In addition to measurements of resonant frequencies at fixed values of the magnetic field valuable information is obtained in nuclear magnetic resonance experiments from studies of line widths, shapes, and relaxation

times. Some of the problems of chemical interest studied by these techniques are mentioned in the following sections.

*Experimental developments.*—The techniques of nuclear magnetic resonance were developed simultaneously and independently by groups at Harvard (7) and at Stanford (5, 6). Much of the work has been done using bridge circuits which may be arranged with amplitude or phase unbalance to produce either an absorption curve or a dispersion curve with the output proportional to either the real or the imaginary part of the magnetic susceptibility.

Certain advantages as search instruments are possessed by "nonbridge" radiofrequency spectrometers (28, 35, 41) which are quite similar to the instruments used in direct quadrupole spectroscopy.

*Chemical shifts.*—The high resolution possible in magnetic resonance experiments has shown that the nuclear magnetic resonance frequency of a particular nucleus in a given external field depends significantly on the kind of molecule in which the nucleus finds itself. The theory of magnetic shielding has been developed by Ramsey (31, 32) but detailed calculations for polyatomic molecules are difficult. Gutowsky & Hoffman (11) have made a detailed survey of magnetic shielding in fluorine and hydrogen compounds. It was found that the magnetic shielding effects in the fluorine compounds were proportional to the difference in electronegativity of fluorine and the atom to which it was chemically bonded. Gutowsky *et al.* (13) defined a new magnetic shielding parameter,  $S = [(H_r - H_c)/H_r] \times 10^6$  where  $H_r$  is the field required for resonance in fluorobenzene and  $H_c$  is the field required for resonance in a substituted fluorobenzene. This quantity was found to be directly proportional to Hammett's sigma factor for a variety of substituent groups. (Compare the results of Wilson in the section on direct quadrupole spectroscopy.)

Early qualitative and exploratory work on magnetic shielding was done by Dickinson (9) and by Proctor & Yu (29). Arnold, Dharmatti & Packard (4) using a nuclear induction apparatus with a resolution of better than one part in  $10^7$  observed magnetic shift and fine structure effects in a number of aliphatic alcohols. Different lines were obtained for H in OH, CH<sub>2</sub>, and CH<sub>3</sub> groups. The areas of the observed absorption lines were proportional to the number of hydrogens of that type in the molecule.

The "spin echo" method developed by Hahn (16) has also been used to investigate magnetic shielding and fine structure phenomena. Beat patterns were observed for a number of chemical systems, among them being C<sub>2</sub>H<sub>5</sub>OH, mixtures of CF<sub>3</sub>CCl=CCl<sub>2</sub> and 1,4-difluorobenzene, and of CF<sub>3</sub>CCl=CCl<sub>2</sub> and 1,2,4-trifluorobenzene. Other papers on magnetic shielding are (13, 14, 24).

*Crystal structure.*—Pake (27) has obtained information on the crystal structures of gypsum, borax, Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O and KF·2H<sub>2</sub>O from studies of the width, shape, and fine structure of proton resonances in these crystals. In CaSO<sub>4</sub>·2H<sub>2</sub>O the distance between protons in the water molecules

was found to be  $1.58 \text{ \AA}$ . Gutowsky *et al.* (12) have used similar techniques to study a number of crystals. The H—H distance in the  $-\text{CH}_2\text{Cl}$  group in 1,2-dichloroethane was found to be  $1.71 \pm 0.02 \text{ \AA}$ . This seems to indicate that the H—C—H bond angle is smaller than the tetrahedral value. Data on ammonium halide molecules gave a value of  $1.025 \pm 0.005 \text{ \AA}$  for the N—H distance in the ammonium ion. Other data on 1,1,1-trichloroethane, perfluoroethane, and diborane were obtained.

Richards & Smith (34) have studied proton resonances in the crystalline monohydrates of nitric, perchloric, and sulfuric acids as well as the dihydrate of oxalic acid at  $90^\circ\text{K}$ . They found that the first three acids contained the oxonium ion but oxalic acid did not. The H—H distance in the oxonium ion for the nitric acid monohydrate was  $1.72 \pm 0.02 \text{ \AA}$  which is consistent with a pyramidal shape and an O—H length of about  $1.02 \text{ \AA}$ . Similar results for perchloric acid were obtained by Kakiuchi *et al.* (21).

Smith & Richards (38) have used the same techniques to study crystals of  $(\text{H}_2\text{O})_2\text{PtCl}_6$ ,  $(\text{H}_3\text{O})\text{HSeO}_4$ , and  $\text{K}(\text{H}_4\text{B}_6\text{O}_{10}) \cdot 2\text{H}_2\text{O}$ .

In general the study of nuclear magnetic resonances offers itself as a method of obtaining accurate proton distances in crystals. The method is best suited for investigating detailed features of crystals whose gross structures have already been determined.

*Phase transitions and hindered internal motion in solids.*—Alpert (1) investigated the mechanisms of phase transitions in solids using nuclear magnetic resonance techniques. The basic factor in experiments of this sort is the dependence of the resonance line width on the average time that is necessary for a molecule to change its orientation appreciably. Alpert's experiments favored an order-disorder mechanism for the transitions in solid HCl, HBr, HI,  $\text{H}_2\text{S}$  and  $\text{H}_2\text{Se}$ .

Gutowsky & Pake (15) have made a thorough study of the temperature dependence of the line widths of the proton resonances of a large number of hydrogen containing compounds. They conclude that in these molecules light symmetrical groups can rotate about their figure axes, even when attached to a heavier framework, at temperatures as low as  $100^\circ$  to  $150^\circ$  below their melting points. Barriers to internal rotation, such as that existing in 1,1,1-trichloroethane, seem to prevent such motions from persisting to such extremely low temperatures.

Holroyd *et al.* (20) have used proton resonance experiments to study transitions in polymers. Line widths obtained for Hevea and G R-S rubbers were very narrow indicating a large degree of "quasi-free rotation" in these substances. Vulcanization, carbon loading, co-polymerization and crystallization produced a broadening of the lines due to the hindrance to internal motions which these factors introduce. Other studies of internal motions in solids are Newman's (24) work on polyethylene, Andrew & Eades' (3) study of cyclohexane, and of Andrew on some solid aromatic hydrocarbons (2).

*Chemical analysis.*—In a number of studies nuclear magnetic resonance

has been used as a tool for chemical analysis. Newman & Ogg (25) measured relaxation times for proton resonances in dilute sodium-liquid ammonia solutions to determine the concentration of paramagnetic solute. They found evidence for an associative equilibrium between paramagnetic and diamagnetic solute species with the paramagnetic solute about one-tenth as effective as cupric ion in inducing nuclear relaxation.

Using a somewhat similar technique with a nuclear induction spectrometer Spooner & Selwood (40) and Selwood & Schroyer (37) have investigated proton relaxation times of water in contact with supported paramagnetic catalysts. They have determined the accessibility of the solid catalysts, defined as the ratio of the activity shown by a fixed weight of solid catalyst to that of the same weight of catalyst in true solution in the reacting medium. Rocher (36) has done similar experiments with  $\text{Al}_2\text{O}_3$  catalysts.

Hickmott & Selwood (19) have studied the kinetics of the reaction  $\text{Eu}^{+3} + e \rightarrow \text{Eu}^{+2}$  making use of some results of Conger & Selwood (8) on proton resonances in solutions of paramagnetic ions.

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# MAGNETISM<sup>1</sup>

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## INTRODUCTION

This article will be concerned with magnetic susceptibilities and specific magnetizations as applied to the solution of chemical problems. The areas of nuclear and paramagnetic resonance will be described elsewhere. Out of the great mass of magnetic data published in recent years there have been chosen four topics for as full discussion as is possible within the limits of space available. Two other topics are treated briefly. The four topics are: (a) magnetic anisotropy of oriented polymer molecules; (b) organic free radicals; (c) the actinides; and (d) catalytically active solids. The two topics chosen for briefer treatment are: (e) coordination compounds, and (f) ferromagnetism and antiferromagnetism. Throughout the review an effort has been made to bring the reader up to date on the present status of the subject and to point to the unsolved problems now confronting us. If the writer seems in what follows to be concerned chiefly with developments in his own laboratory, he must shift the blame to the substantial group of research students whose ingenuity in solving old problems is only matched by their persistence in raising new ones.

## MAGNETIC ANISOTROPY

In crystals of low symmetry there are found three mutually perpendicular directions known as the axes of principal magnetism. Along these axes the direction of magnetization corresponds with the direction of the applied field. The susceptibilities along these axes are referred to as principal magnetic susceptibilities and are often unequal. Gases and liquids are, of course, isotropic. If an anisotropic crystal is powdered the average susceptibility of the powder becomes the mean of the three principal susceptibilities.

Crystals of aromatic organic compounds show a large magnetic anisotropy (as does graphite). The influence of neighboring molecules on the susceptibilities of diamagnetic molecules is negligible. Hence crystal anisotropy must be due to the resultant anisotropy of the individual molecules in the unit cell. If the molecule is isotropic, then the crystal will show little or no anisotropy, but if the molecule is anisotropic then the anisotropy of the crystal depends on the relative orientation of the molecules. It follows that a measurement of magnetic anisotropy may aid, in crystals of low symmetry, in determining molecular orientations.

The method of magnetic anisotropy has been used in many investigations

<sup>1</sup> The survey of the literature pertaining to this review was concluded in December, 1952.

of structure in organic compounds by Krishnan and by Lonsdale and others, (1, 2, 3). The method will be outlined briefly by reference to biphenyl, an example given by Lonsdale & Krishnan. The principal molar susceptibilities for the benzene molecule are  $K_1 = -37.3$ ,  $K_2 = -37.3$ , and  $K_3 = -91.2$  ( $\times 10^{-6}$ ). Subtracting  $-7.7 \times 10^{-6}$  for the two hydrogens, one obtains for biphenyl  $K_1 = K_2 = -66.9$ ,  $K_3 = -174.7$ . The principal molar susceptibilities for biphenyl crystal are found to be  $\chi_1 = -63.4$ ,  $\chi_2 = -146.5$ , and  $\chi_3 = -98.9$ . The angle  $\psi$  between  $\chi_1$ , and the  $c$  axis, is  $20.1^\circ$ . There are two molecules in the unit cell; place both with their planes parallel to (100) and their lengths along the  $c$  axis, then give the molecules the following orientations: rotate one molecule about the  $c$  axis through an angle  $\lambda$ , and the other through  $-\lambda$ . Rotate both molecules about the  $b$  axis through an angle  $\delta$ . Rotate both molecules through  $+\nu$  and  $-\nu$  respectively about the normal to the plane which contains the  $b$  axis and the direction of lengths of the molecules after the second rotation. Then  $\delta = \psi = 20.1^\circ$  and  $\lambda$  and  $\nu$  can be obtained as follows:

$$\chi_1 = K_1 \cos^2 \nu + (K_2 \cos^2 \lambda + K_3 \sin^2 \lambda) \sin^2 \nu$$

$$\chi_2 = K_2 \sin^2 \lambda + K_3 \cos^2 \lambda$$

$$\chi_3 = K_1 \sin^2 \nu + (K_2 \cos^2 \lambda + K_3 \sin^2 \lambda) \cos^2 \nu$$

As  $\chi_1 + \chi_2 + \chi_3 = K_1 + K_2 + K_3$ , only two of the above are independent. Hence, solving  $\lambda = 31^\circ$  and  $\nu = 0^\circ$ , The lengths of the molecules lie in the (010) plane at  $20.1^\circ$  to the  $c$  axis, while the planes of the molecules are inclined at plus and minus  $31^\circ$ , respectively, to the  $b$  axis. It should be pointed out that this structural determination is a rather ideal case and that with increasing crystal symmetry the method becomes of diminishing value.

Aromatic compounds show large molecular magnetic anisotropies, the largest diamagnetism being perpendicular to the plane of the ring. The usual explanation for this is that in such compounds (and in graphite) the diamagnetic currents are not limited to individual atoms, but circulate from one atom to another in relatively extended orbits. In benzene, for example, it is thought that the effective radius of the  $\pi$  electrons, which take part in conjugation, is more nearly that of the whole molecular ring, rather than that of an individual atom. Reasonably satisfactory theories of this effect have been developed by London (4), Pauling (5), and others, but there is as yet no very satisfactory explanation for the existence of a large diamagnetic susceptibility normal to the plane of the conjugated bonds in open chain molecules as well as in aromatic rings.

The existence of molecular magnetic anisotropy, and the relatively large effects shown by aromatic groups, suggests use of the method in studying orientation in high polymers such as polystyrene. The method has been applied to polythene, various polystyrenes, to polyethylene terephthalate and to a variety of natural and synthetic rubbers (6, 7, 8). The experimental arrangement will first be described briefly.

The sample under investigation is suspended by a fine torsion fiber in a

homogeneous field of five to ten thousand oersteds. If an anisotropic sample is suspended so that one magnetic axis is parallel to the torsion fiber, then the sample will turn until the largest (algebraic) susceptibility in the plane of rotation approaches the direction of lines of force. The torsion head may now be turned until the crystal suffers no orientating effect on application of the field. There are two alternative methods for finding the magnetic anisotropy in the plane of rotation of the sample. The method known as Krishnan's second, or "flip-angle," method is the more convenient and will be described. The torsion head is now turned through an angle  $\alpha$ . This will cause the sample to turn through a smaller angle  $\phi$ . If rotation of the torsion head is continued to  $\alpha_e$  until  $\phi = \pi/4$  radians, the sample will suddenly flip around to a new equilibrium position. This will occur when  $C(\alpha_e - \pi/4) = mH^2(\chi_1 - \chi_2)/2M$ , where  $m$  is the mass of the sample,  $H$  the field,  $\chi_1$ ,  $\chi_2$  the principal susceptibilities in the plane of rotation of the sample, and  $M$  the molecular weight of the sample.

Drawn fibers resemble uniaxial crystals in that only one sample orientation is necessary, namely that in which the symmetry axis is perpendicular to the torsion fiber. The anisotropy measured is then  $\chi_{||} - \chi_{\perp}$ , the difference in principal susceptibilities parallel to and perpendicular to the symmetry axis. The anisotropy may be measured as a function of composition, draw ratio, heat treatment, and so forth. Often it may be necessary to prepare bundles of fibers for measurements on thin filaments. Often it is instructive to obtain, where possible, the molecular anisotropy of the repeating unit in the polymer. This may sometimes be done by study of the nearest simple analogue as, for instance, dimethyl terephthalate in connection with studies on polyethylene terephthalate. In this way there is some promise of evaluating molecular orientation in a substantially amorphous polymer. Examples are given below for such investigations on polyethylene, polystyrene, substituted polystyrenes, polyethylene terephthalate, and a variety of natural and synthetic rubbers.

Polyethylene contains no aromatic groups and hence is expected to show, even in highly drawn samples, only a small magnetic anisotropy which has been shown to have the largest diamagnetism parallel to the long axis of the molecule. A drawn fiber of polyethylene will thus tend to set itself perpendicular to the lines of force in a homogeneous field. The maximum anisotropies ( $\chi_{||} - \chi_{\perp}$ ) observed by Weir & Selwood did not exceed  $2.8 \times 10^{-6}$  per mole of repeating (ethylene) group. On the other hand, polystyrene at 980 per cent elongation has an anisotropy of  $5.3 \times 10^{-6}$  per repeating unit while poly-2,5-dichlorostyrene at 500 per cent elongation has an anisotropy of  $22.3 \times 10^{-6}$  per repeating unit. In both polystyrenes the maximum diamagnetism is parallel to the fiber axis.

In the polystyrenes the largest contribution to the magnetic anisotropy is made by the aromatic groups, and since the largest diamagnetic susceptibility in aromatic groups is perpendicular to the plane of the rings, it follows that the aromatic groups in both styrenes have a preferred orientation such



that the normal to the plane of each ring tends to be parallel to the fiber axis. It is clear from molecular models that the rings must lie perpendicular, or nearly so, to the long axis of the polymer chain in both polystyrenes. But the requirement that the normal to the plane of each ring should be parallel to the chain axis is not necessarily fulfilled. In polystyrene the observed anisotropy suggests that the rings may rotate around the carbon-carbon bond with less than free rotation, but in the polydichlorostyrene this rotation about the bond joining the ring to the chain must be much less because the chlorine atom in the 2-position restricts rotation to a few degrees on either side of the perpendicular.

From a knowledge of the anisotropy in polyethylene, and the principal molecular susceptibilities of the phenyl group and the 2,5-dichlorophenyl group, Weir & Selwood have calculated the maximum anisotropy to be expected if all rings are oriented with the normal to the plane of the rings strictly parallel to the fiber axis. Comparison of these values with observed results shows that unoriented polystyrene shows only a negligible 1.5 per cent of the maximum theoretical anisotropy, stretched polystyrene shows 9.5 per cent, and stretched poly-2,5-dichlorostyrene shows 40.5 per cent. These results are in agreement with those obtained from x-ray diffraction. The method has obvious applications to other high polymers containing aromatic groups.

Magnetic anisotropy studies on polyethylene terephthalate differ chiefly in that as the aromatic groups are in the chain, complete orientation should cause all rings to lie with their planes parallel to the fiber axis, but with the normals to the planes of the rings at all possible orientations perpendicular to the fiber axis. The largest algebraic susceptibility in highly stretched polyethylene terephthalate should therefore lie in the fiber axis rather than perpendicular to it as was the case for the polystyrenes. This conclusion is confirmed by experiment, the observed anisotropy being roughly the difference between the principal susceptibility of a benzene ring parallel to the plane and the average of the principal susceptibilities parallel and perpendicular to the plane of the ring, as predicted. Amorphous or polycrystalline polymer without preferred orientation is, as expected, isotropic. It is interesting that with increasing fiber elongation the magnetic anisotropy does not increase linearly, but rather remains low and then increases abruptly at a certain critical percentage elongation.

Magnetic studies on stretched elastomers are more difficult because of the necessity for keeping the samples under tension while the rather delicate measurements are in progress. Toor & Selwood have investigated several natural and synthetic rubbers under various conditions of elongation. As expected, all rubbers develop some magnetic anisotropy on stretching. Unsaturated rubbers develop a fairly large principal susceptibility perpendicular to the direction of stretching. This is to be expected from the presence of olefinic double bonds. The anisotropy is less (as in polybutadiene) where ever cross-linking hinders alignment of the long-chain molecules parallel to

the direction of stretching. Saturated stretched rubbers have a small anisotropy opposite in sign to that of unsaturated rubbers.

#### FREE RADICALS

Ever since the first demonstration of paramagnetism in a free radical by Taylor in 1926 there has been a growing confidence that the magnetic susceptibility, although not easy to measure, offered reliable qualitative and quantitative information concerning these substances. A substantial number of free radicals has been investigated and reported on during the past twenty years, chiefly by Müller, Marvel, Michaelis, and by the writer. At the present time, however, there is reason to believe that degree of dissociation calculations based on the susceptibility of hexaarylethanes and related compounds may be subject to a large systematic error. The nature of this error will be described.

There will first be reviewed the usual method for calculating the degree of dissociation of a hexaarylethane from a susceptibility measurement on a solution containing the ethane and free radicals, it being assumed that other substances are absent although this is not always true. The percentage of ethane is found from the weights of solvent and chloromethane used in making up the solvent. The susceptibility of the ethane may then be found by assuming, probably correctly, that the susceptibilities of ethane and solvent are additive. From the molar susceptibility of the partly dissociated ethane subtract its diamagnetism which may be found from Pascal's constants; this step gives the paramagnetic susceptibility produced by the free radicals. Finally, the degree of dissociation is found by dividing the molar paramagnetism found as above by the molar paramagnetism expected, at the temperature used, for one mole of ethane completely dissociated into free radicals.

Some difficulties have arisen with respect to the results obtained by the calculation outlined above. For instance, solutions of the Chichibabin hydrocarbon, although highly reactive and strongly colored, have been reported by Müller on the basis of susceptibility measurements as being not over 2 per cent dissociated, but Schwab's *ortho-para* hydrogen conversion on solutions of this substance suggest about 10 per cent dissociation. There is also the difficulty that hexa-*p*-biphenylethane seems, on the basis of magnetic measurements, to be less dissociated in solution than in the pure crystalline solid. Selwood & Dobres (9) have reported that this ethane in solution appears, on the basis of color and apparent heat of dissociation, to be completely dissociated, but the susceptibility measurements indicate only about 70 per cent dissociation. Similar results are reported on hexa-*p-tert*-butylphenylethane.

An explanation for these anomalies is possibly to be found in the diamagnetic correction which is implicitly assumed to be the same for the free radicals as for the undissociated ethane. The validity of this assumption has been questioned previously, and Selwood & Dobres point out that resonance

stabilization of the free radical might lead to an enhanced diamagnetism perpendicular to the plane of the radical molecule. Another way of stating this is that the additional resonance in the radical might give a greatly increased magnetic anisotropy over that normally found in isolated aromatic rings. The susceptibility data on hexa-*p*-biphenylethane would yield reasonable results if the underlying diamagnetism of the radical were to be increased by 80 per cent. This would mean a 240 per cent increase in the principal susceptibility normal to the plane of the rings.

Unfortunately for this explanation, the only published attempt to find a theoretical basis for such an enhanced diamagnetism has led to results in the opposite direction. Pullman & Berthier (10) have shown that, at least in the systems studied, conjugation between aromatic and aliphatic groups tends to lower the magnetic anisotropy. In nonradical molecules this theoretical prediction is supported by experimental evidence.

The state of the problem at the moment is that doubt has been placed on the quantitative application of magnetic susceptibilities to free radicals of the triarylmethyl type. Apart from the desirability of clearing up this situation for its own sake there is the equally interesting problem of finding the influence, if any, of free radical formation on the underlying diamagnetic anisotropy of the molecule.

#### THE ACTINIDES

The actinide hypothesis, namely the view that the heaviest atoms form a second "rare earth" series containing 5*f* electrons, has led to such practical successes and is supported by so much chemical and physical evidence, that a certain distaste has arisen for any evidence of a contrary nature. This must be the reason why several groups of workers, having magnetic evidence on uranium and plutonium compounds which obviously could be interpreted either way or else favored the 6*d* electron configuration, chose to claim that magnetic evidence likewise confirmed the 5*f* view. This is doubly regrettable because this view has tended to become accepted without further question.

Thanks chiefly to the work of Dawson (11) it is now possible to allocate electrons among the actinides with considerable precision and to see that under certain conditions there is strong evidence for the 6*d* configuration. Some of the earlier work will be reviewed. This will be followed by a discussion of Dawson's several papers.

Most early work on uranium was done at room temperature, or on such compounds as the oxide, in which the possibility of exchange effects could not be ignored. It was impossible to say on the basis of measurements on uranium dioxide, for instance, whether the magnetic properties of uranium (+4) more closely resembled those of the rare earths, or of the group VI elements chromium, tungsten, and molybdenum. Studies of the temperature coefficient of susceptibility on uranium tetrafluoride give a magnetic moment of 3.3 Bohr magnetons and a Weiss constant of  $\sim 116^\circ$ . Similar measurements on uranium (+4) sulfate, oxalate, and acetylacetonate yield

moments of 3.52, 3.75, and 3.21 with the corresponding Weiss constants of  $113^\circ$ ,  $168^\circ$ , and  $101^\circ$ . These data have been interpreted as proving the existence of 5f electrons in the uranium. But such large values of the empirical Weiss constant in such magnetically dilute compounds as the last two mentioned simply indicates the inapplicability here of the simple theory which serves for the first transition series and for the rare earths. Similarly, data on neptunium and plutonium ions have been interpreted as establishing the 5f configuration. But these data were obtained at one temperature only, and the moments were calculated by a method equivalent to assuming a Weiss constant of zero. Others have reached the same conclusion by the use of Weiss constants in excess of  $100^\circ$ . The absurdity of these procedures will be clear when it is considered that a moderate change of Weiss constant can lead to totally different conclusions concerning the distribution of electrons in these elements.

A rare earth element yields substantially the same magnetic moment no matter what compound is used for study. This is true because of the well known sequestration of the 4f electrons. But elements of the first transition series, such as chromium, give apparent moments which vary quite widely depending on what compound is under investigation. This is simply another way of saying that the apparent moment of an ion in the first transition series is often strongly dependent on the ionic environment. The reasons for this are two-fold. First, for several of these ions, although probably not for  $\text{Cr}^{+3}$ , the spin-orbital coupling is partially broken down by the field of surrounding ions or oriented dipoles. In nickel and cobalt salts, for instance, the degree of orbital quenching varies from substance to substance with an attendant variation of apparent moment. On the other hand, those ions such as  $\text{Fe}^{+3}$  and  $\text{Mn}^{+2}$  which are in S states show moments substantially independent of ionic environment provided that the environment is magnetically dilute and can truly be considered ionic.

The second reason for dependence of apparent moment on environment in the first transition series has to do with exchange effects which occur whenever paramagnetic ions are closely packed together. These effects are almost negligible in the rare earths but are so strong in familiar oxides such as  $\text{Cr}_2\text{O}_3$  and  $\text{CuO}$  as to reduce the susceptibility to a small fraction of that to be expected for the ions  $\text{Cr}^{+3}$  and  $\text{Cu}^{+2}$  respectively. These exchange effects, as is well known, sometimes give rise to ferromagnetism, but more frequently, as in the cases mentioned, give rise to antiferromagnetism. If exchange effects are appreciable there is no reason to believe that the apparent magnetic moments observed will have any simple relation to electron distribution in the ions. The simple theory of paramagnetism as developed by Van Vleck does not take exchange effects into account, and a survey of data on various oxides and other magnetically concentrated substances such as fluorides will show how erratic and confusing the apparent moments can be.

There is, fortunately, a method by which these difficulties may be overcome. The paramagnetic substance under investigation is prepared in dilute

solid solution in a diamagnetic substance with which it is isomorphous and in which the positive ion has approximately the same radius. This method of "diamagnetic isomorphous dilution" seems first to have been used by Bizette (12) in a study of the system  $\text{MnO-MgO}$ . With increasing dilution the susceptibility of the manganese rises rapidly, the antiferromagnetic Curie point ( $\sim 115^\circ\text{K.}$ ) disappears, the Weiss constant above the Curie point diminishes to near zero, and the magnetic moment of the manganese ( $+2$ ) ion becomes exactly that expected (5.9) for five unpaired electrons, with "spin-only" moments effective.

Dawson (13) and others (14) have used this method for the systems  $\text{UF}_4\text{-ThF}_4$ ,  $\text{UO}_2\text{-ThO}_2$ ,  $\text{PuF}_4\text{-ThF}_4$ , and  $\text{PuO}_2\text{-ThO}_2$ ; the  $\text{Th}^{+4}$  ion fortunately fulfilling the requirements of diamagnetism and ionic radius. For the systems containing uranium the results show that  $\text{U}^{+4}$  is capable of showing fairly large exchange effects. These are much larger than is found say in neodymium oxide, but smaller than in  $\text{Cr}_2\text{O}_3$ . The Weiss constant, which in most of these magnetically concentrated systems is related solely to exchange effects, falls, in  $\text{UO}_2$  from over  $200^\circ$  to zero with increasing dilution with  $\text{ThO}_2$ . The magnetic moment of the  $\text{U}^{+4}$  ion under these conditions of magnetic dilution falls from about 3.2 to 2.8 Bohr magnetons, namely to exactly the moment expected for two "spin-only"  $6d$  electrons. Dawson has obtained exactly parallel results on the system  $\text{UF}_4\text{-ThF}_4$  (an earlier report by Dawson, later corrected, gave a different result). As Dawson says: the technique of dilution in solid solution with an isomorphous diamagnetic compound and extrapolation of the susceptibilities to infinite dilution provides a means for better assessment of the electron configuration, the result being not necessarily the one expected on the basis of measurements on the undiluted compounds.

Dawson's measurements on sodium plutonyl acetate show likewise that the ground state of the plutonyl ion has a  $6d^2$  electron configuration. These results, together with those on uranium, are taken to show that in those ions of the actinides which have two unpaired electrons, the  $6d$  appears to be considerably more stable than the  $5f$  energy level.

On the other hand, Dawson's results on the systems  $\text{PuO}_2\text{-ThO}_2$  and  $\text{PuF}_4\text{-ThF}_4$  show that for the latter system the  $5f^4$  configuration is definitely preferred, while for the oxide system some of the evidence favors a  $5f^3\cdot 6d$  configuration. The conclusion from magnetic studies on these elements is, therefore, that the actinides show exchange effects which place them midway between the rare earths and the first transition series, and that the actual distribution of electrons in these elements varies from  $5f$  to  $6d$  and is a function of number of electrons and probably also of ionic environment.

#### CATALYTICALLY ACTIVE SOLIDS<sup>2</sup>

The principal applications of magnetism to catalysis are like the applications of x-rays and electron diffraction. Magnetic susceptibilities and related

<sup>2</sup> The present reviewer has published an earlier review on the topic "Magnetism and the Structure of Catalytically Active Solids," covering the literature through August, 1949 (15).

quantities serve as tools for structural identification of the catalyst. These methods are most useful for those substances which, like chromia gel, are paramagnetic or which, like the iron carbides, are ferromagnetic. The paramagnetic substances will be discussed here, with some reference to ferromagnetic catalyst components and thermomagnetic analysis in a later section.

It is characteristic of catalytically active solids that they may often be prepared in a form having high specific surface and high activity. Chromia gel, mentioned above, is one example of such a substance. The amorphous nature of these substances makes them difficult to study by the usual methods of structural investigation, such as x-ray diffraction. For this reason, there is still little agreement as to the structural nature of this large and important group of substances, which are often referred to as gels.

Some years ago it was found that the paramagnetic gels (16) have magnetic properties which sharply distinguish them from the same substance in the more familiar crystalline form. Thus, the chromium ions in chromia gel have a susceptibility which follows the Curie-Weiss law over a fairly large temperature interval, with a normal moment for three electron spins, and with a Weiss constant of roughly  $100^\circ$ . By contrast, crystalline chromia is a typical antiferromagnetic with a susceptibility only slightly dependent on temperature and with a low maximum, corresponding to the antiferromagnetic Curie point at about  $50^\circ\text{C}$ . A similar magnetic relation between the active gel form and the relatively inactive crystalline form is found for most of the transition group oxides such as  $\text{VO}_2$ ,  $\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$ , and  $\alpha\text{-Fe}_2\text{O}_3$ . It will be clear that at low temperatures, well below the antiferromagnetic Curie point, the susceptibility of the gel may be many times greater than that of the same substance in crystalline forms.

Above the Curie point the chief magnetic difference between gel and crystal lies in the magnitude of the Weiss constant which for a typical chromia gel may be  $100^\circ$  and for the crystal is about  $300^\circ$ . An early theory of antiferromagnetism gave the Weiss constant, as  $-\Delta = 2JzS(S+1)/3k$  where  $J$  is the exchange integral,  $z$  the number of nearest paramagnetic neighbors,  $S$  the spin quantum number, and  $k$  the Boltzmann constant. Hence, assuming  $J$  to be the same in gel and crystal, we may write  $z_{\text{gel}} = z_{\text{cryst}} \Delta_{\text{gel}}/\Delta_{\text{cryst}}$  from whence the number of nearest chromium neighbors possessed by each chromium ion in the gel may be calculated. With this information it is possible to make a model of the gel, and one reaches the conclusion that the gel must be extraordinarily attenuated into virtually monatomic sheets or perhaps into threads no more than a few Ångströms thick. But this latter view is the one held by colloid chemists concerning the structure of some gels; and the high degree of attenuation is supported by the large observed specific surfaces which, in chromia gel, may reach  $600 \text{ m}^2/\text{gm}$ .

The crudeness of this interpretation of the magnetic data will be obvious. The attempt is, however, justified by the urgent need for more structural information concerning catalytically active solids. The development of a new and expanded theory of antiferromagnetism (17), with its emphasis



on second nearest neighbors, suggests an avenue of approach to this problem and it is to be hoped that someone reading this paragraph will be inspired to solve the problem.

Catalytically active solids are often prepared in a form referred to as "supported." A familiar example is the chromia-alumina dehydrocyclization catalyst which may be prepared by the impregnation of high-area "gamma" alumina with a solution containing chromium, followed by drying, ignition, and reduction. This procedure might be expected to produce a system in which the particles of alumina are more or less uniformly covered with microcrystals of chromia. Little is known concerning the surface structure of such catalysts because, in the most useful concentration range, they show no x-ray diffraction pattern for any substance other than the support. It has been found, however, that magnetic measurements give some information concerning degree of dispersion of the supported oxide (18). In supported catalysts the promoter concentration may generally be varied within wide limits by varying the concentration of the solution used in the impregnation step. Catalysts prepared in this way show large differences in magnetic susceptibility per gram of promoter. For instance, the susceptibility per gram of copper in a cupric oxide supported on high-area alumina is many times larger than that of copper in pure crystalline copper oxide (19). These differences become increasingly great at low temperatures. In many supported oxide systems the susceptibilities have been related to increasing dispersion with lower promoter concentration. The catalyst surface has been shown, at low promoter concentrations, to consist of isolated, widely separated, promoter aggregates, separated by bare support surface. In some cases it has proved possible to predict the relative activity of two catalysts on the basis of magnetic susceptibility measurements alone (20). In certain cases, such as that of supported oxides of manganese, the support surface has been shown to exert an inductive effect on the oxidation state of the promoter, thus favoring  $Mn_2O_3$  on  $Al_2O_3$ , but  $MnO_2$  on  $TiO_2$  (21). In spite of its proved usefulness in the study of such materials, it must be said that the quantitative understanding of magnetic susceptibilities in relation to catalyst structure still leaves much to be desired.

A somewhat different field of application for magnetism in catalysis is in connection with metals and alloys as exemplified in a paper by Dowden (22). Recent reviews on heterogeneous catalysis have emphasized the increasing importance of the "electronic factor," which may be described, somewhat inadequately, as the number of electrons available for interaction with an absorbed molecule of reactant, and the energetics associated with those electrons. The magnetic application is chiefly to find the number of such available electrons.

Many catalysts of importance have almost filled, or just filled  $d$ -bands, and activity is found to vary in a rapid and predictable way among these elements. The magnetic moment is a measure of  $d$ -band filling, hence catalytic

activity and magnetism are actually in part different manifestations of a more fundamental property, namely, the *d*-band character of the element.

These ideas apply also to alloys (23, 24). If an element with loosely held valency electrons, such as copper, is added, in solid solution, to a transition element possessing holes in the *d*-band, such as nickel, the change in activity parallels the decline in number of holes per nickel atom. There is a simultaneous gradual loss of ferromagnetism of the nickel alloy with increasing copper content. It is thus possible to predict relative catalytic activities on the basis of magnetic measurements in favorable cases. But it must be understood that *d*-band character is by no means the only criterion of catalytic effectiveness. Specific surface area and other factors play an equally important role.

It has also been shown that catalyst poisons may operate by a related process, namely, filling of all *d*-band holes by electrons supplied by the poison (25). Thus the loss of paramagnetism by palladium on exposure to hydrogen probably is caused by filling of the *d*-band holes in the palladium. This may account for a number of obscure examples of catalyst poisoning by hydrogen. Similarly, methyl sulfide, a catalyst poison, reduces the susceptibility of surface palladium atoms to zero (26).

#### COORDINATION COMPOUNDS

In recent years determination of magnetic moments of transition elements present in coordination compounds has been one of the most active branches of magnetochemistry. It has, of course, been known for a long time that an element such as iron in a coordination complex might show a magnetic moment quite different in different types of complex. Thus iron in ferric ammonia complexes has a moment of about six Bohr magnetons, while that in a ferricyanide is only about two magnetons. Stimulation of interest in this field dates from Pauling's papers (27), in which he related magnetic moment to bond type and to the stereochemistry of the complex. Nearly all magnetic studies on coordination complexes since that time have been related to Pauling's interpretation. In view of the peculiarly unsatisfactory condition of this subject at the present time, the original Pauling interpretation will first be reviewed briefly.

Electrons used in covalent bond formation contribute nothing to the permanent magnetic moment of the complex. Unpaired electrons in elements of the first transition series generally contribute to the moment in accordance with the "spin-only" formula  $\mu = \sqrt{n(n+2)}$  where  $\mu$  is the moment in Bohr magnetons and  $n$  is the number of unpaired electrons. Hence, from a knowledge of the total number of electrons used in the formation of a coordination complex, and from a knowledge of the magnetic moment as experimentally found, it is possible by subtraction to find the number of electrons used in covalent bond formation. In favorable cases this information may be used to deduce the nature of the orbitals involved and hence the spatial con-



figuration of the complex. For instance, the divalent nickel atom has two unpaired electrons, with a normal spin-only moment of about 2.8 magnetons. In tetrahedral complexes involving ionic bonds the moment remains almost unchanged. But for the formation of four planar  $dsp^2$  covalent bonds there are only four  $3d$  orbitals available for eight electrons. The square, planar nickel complexes such as  $K_2Ni(CN)_4$  are therefore diamagnetic. In this way information may be gained concerning the stereochemistry of the complex, and a determination may be made as to whether the bond type is essentially ionic or essentially covalent.

It has been recognized for some time that the method outlined above has some limitations. Alternative interpretations (28) have been offered by several groups of workers but it has never been possible to decide which interpretation is the most acceptable. Certain practical difficulties have arisen in that for some ions of the transition metals, notably  $Co^{+2}$ , spin-orbital coupling is strong enough to make the spin-only formula useless. It will also be noted that the magnetic criterion of bond-type is actually limited to a very small group of elements because in many, such as  $Cu^{+2}$ , the number of unpaired electrons is the same whether the bonding is ionic or covalent. But in spite of these and other difficulties, magnetic moments of coordination complexes continue to fill the literature.

The present status of the magnetic criterion for bond type in complexes seems to be as follows: (a) In a substantial number of cases the agreement as to bond type is poor when the magnetic criterion is compared with other methods such as exchange reactions and absorption spectra. (b) This and other considerations have led Pauling (29), to abandon his original interpretation in the following words which appeared in 1948:

We conclude accordingly that the magnetic criterion distinguishes, not between essentially covalent bonds and essentially ionic bonds, but between strong covalent bonds, using good hybrid bond orbitals and with the possibility of unsynchronised ionic-covalent bonds, using poor bond orbitals, and the necessity for synchronisation of the covalent phases of the bonds.

While the precise meaning of the above statement eludes this reviewer, some idea of the confusion remaining in the area may be gained by comparing Pauling's words with those of Martell & Calvin (30) who, writing in 1952, point out some of the limitations of the magnetic method, but then conclude that when the method may be applied it will tell us whether the bonds are either "essentially covalent" or "essentially ionic."

Magnetic susceptibilities of coordination compounds are not difficult to measure, and the results are often strikingly characteristic of individual substances. It is greatly to be desired that the interpretation of these results could be put on a satisfactory basis.

## FERROMAGNETISM AND ANTIFERROMAGNETISM

In this section there will be first described some applications of thermomagnetic analysis, followed by remarks on the current status of some theories of ferromagnetism and antiferromagnetism. In spite of the substantial current activity in ferromagnetism it should be pointed out that only a relatively small segment of this interest is of direct concern in the solution of chemical problems.

Thermomagnetic analysis is the use of specific magnetizations and Curie points of ferromagnetic substances as a means of quantitative and qualitative analysis. The Curie point of a ferromagnetic is characteristic of a given substance as is the melting point of an organic compound. The specific magnetization is also characteristic and dependent on the mass of ferromagnetic substance actually present in a sample. Instruments have been described for the automatic recording of specific magnetization as a function of temperature or of time (31, 32). Such devices have proved to be unusually powerful tools, with the unfortunate drawback of being restricted to the rather small number of substances known to be ferromagnetic.

Thermomagnetic analysis has been applied successfully to several problems in the structure of catalytically active solids. Thus the presence of Hägg carbide,  $\text{Fe}_3\text{C}$ , has been demonstrated in a Fischer-Tropsch catalyst under conditions where x-ray diffraction methods may not give unequivocal results (33). When a ferromagnetic substance enters into a solid solution the Curie point is lowered. This effect has been used to investigate the structure of copper catalysts promoted with small amounts of nickel (34). It has been found that in such catalysts the nickel is present as a continuous series of solid solutions ranging from almost pure nickel down to quite dilute nickel-copper solutions. Thermal inactivation of such a catalyst is attended with further dilution of the nickel, although it is probably not the only mechanism by which inactivation may occur. The method of study indicated has applications to the sintering process in powder metallurgy (35).

Possibly the most interesting application of thermomagnetic analysis is in the study of rate processes in the solid state. The method is especially useful for following such reactions as the disproportionation of Hägg carbide (33),  $3 \text{Fe}_3\text{C} \rightarrow 2\text{Fe}_5\text{C} + \text{C}$ ; the decomposition of cobalt carbide (36),  $\text{Co}_2\text{C} \rightarrow 2\alpha\text{-Co} + \text{C}$ ; the disproportionation of the wustite phase corresponding approximately to ferrous oxide (37),  $4 \text{FeO} \rightarrow \text{Fe}_3\text{O}_4 + \text{Fe}$ ; and the phase transition of ferromagnetic gamma ferric oxide to paramagnetic alpha ferric oxide (31). It is a fairly simple matter with a recording thermomagnetic balance to follow these reaction rates at different temperatures or other changing conditions. Such studies may be expected to throw new light on some obscure problems connected with reactions in the solid state.

Recent years have seen some notable advances in theories of ferromagnetism and antiferromagnetism. One of these theories, that of Néel (38), is of particular interest in relation to the chemistry of the solid state, and

especially to ferrites and related substances. An outline of Néel's theory will be given with reference, first, to magnetite.

Examination of a model will show that in magnetite there are two kinds of interstices between oxygen ions. One kind has tetrahedral symmetry with four oxygen neighbors, the other octahedral with six oxygen neighbors. In normal spinels the tetrahedral interstices are occupied by the divalent ions ( $M^{+2}$ ), the octahedral by  $Fe^{+3}$ ; but in inverse spinels, of which magnetite is one, the  $Fe^{+3}$  ions occupy the tetrahedral holes and the divalent ions some of the octahedral.

Néel's theory, in brief, is that the magnetic ions in tetrahedral holes always have a negative spin interaction with neighboring ions in octahedral holes, but that interaction of either type with neighboring ions in the same type of holes will be positive. Magnetite may be written  $FeO \cdot Fe_2O_3$  and, for each  $Fe^{+3}$  in a tetrahedral hole, one  $Fe^{+3}$  and one  $Fe^{+2}$  are present in octahedral holes. The saturation moments (not to be confused with the moments derived from measurements on paramagnetics) are for  $Fe^{+3}$  5 and for  $Fe^{+2}$  4. Each  $Fe_3O_4$  group then contains five electron spins in a tetrahedral setting directed antiparallel to five spins in an octahedral setting. This leaves four spins directed parallel to each other in an octahedral setting with a resulting saturation moment of four magnetons per  $Fe_3O_4$ , but this will be slightly complicated by an underlying antiferromagnetism arising from the antiparallel spins. The observed magnetic behavior of magnetite is in agreement with this prediction. For a ferrite of the composition  $MnO \cdot Fe_2O_3$  the five spins in the  $Mn^{+2}$  ion align parallel to the five spins of the iron in sites of the same kind, but are antiparallel to the five spins from iron in sites of the other kind. This leaves a moment of five magnetons. Zinc ferrite,  $ZnO \cdot Fe_2O_3$ , is diamagnetic because the ten spins in the two iron ions merely oppose each other, the zinc ion itself having no unpaired spins. Such considerations have been extended to numerous spinels and related substances of fairly complicated structure. The theory is of obvious use as an aid to location of the units in spinel-like compounds and to prediction of their properties.

The mechanism of exchange whereby one electron spin may augment or nullify another in a nearby atom has also received attention recently. Van Vleck (17) has shown that in a typical antiferromagnetic such as  $MnO$  the nearest manganese neighbors are rather too far from each other to permit direct exchange, and they are situated with respect to an oxygen ion so that superexchange through the oxygen must take an unlikely right-angled path. This observation has led to the conclusion that the most probable path for superexchange in this substance is through an oxygen lying on the direct line between the second nearest manganese neighbors. If this view can be established and extended to slightly more complex substances, it may have

applications in solving the structure of the amorphous solids of catalytic interest described earlier in this report. A possible example of superexchange leading to ferromagnetism rather than to antiferromagnetism is found in the mixed crystals of lanthanum hypomanganite,  $\text{LaMnO}_3$ , and various manganites such as  $\text{CaMnO}_3$ , as described by Jonker & van Santen (39).

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